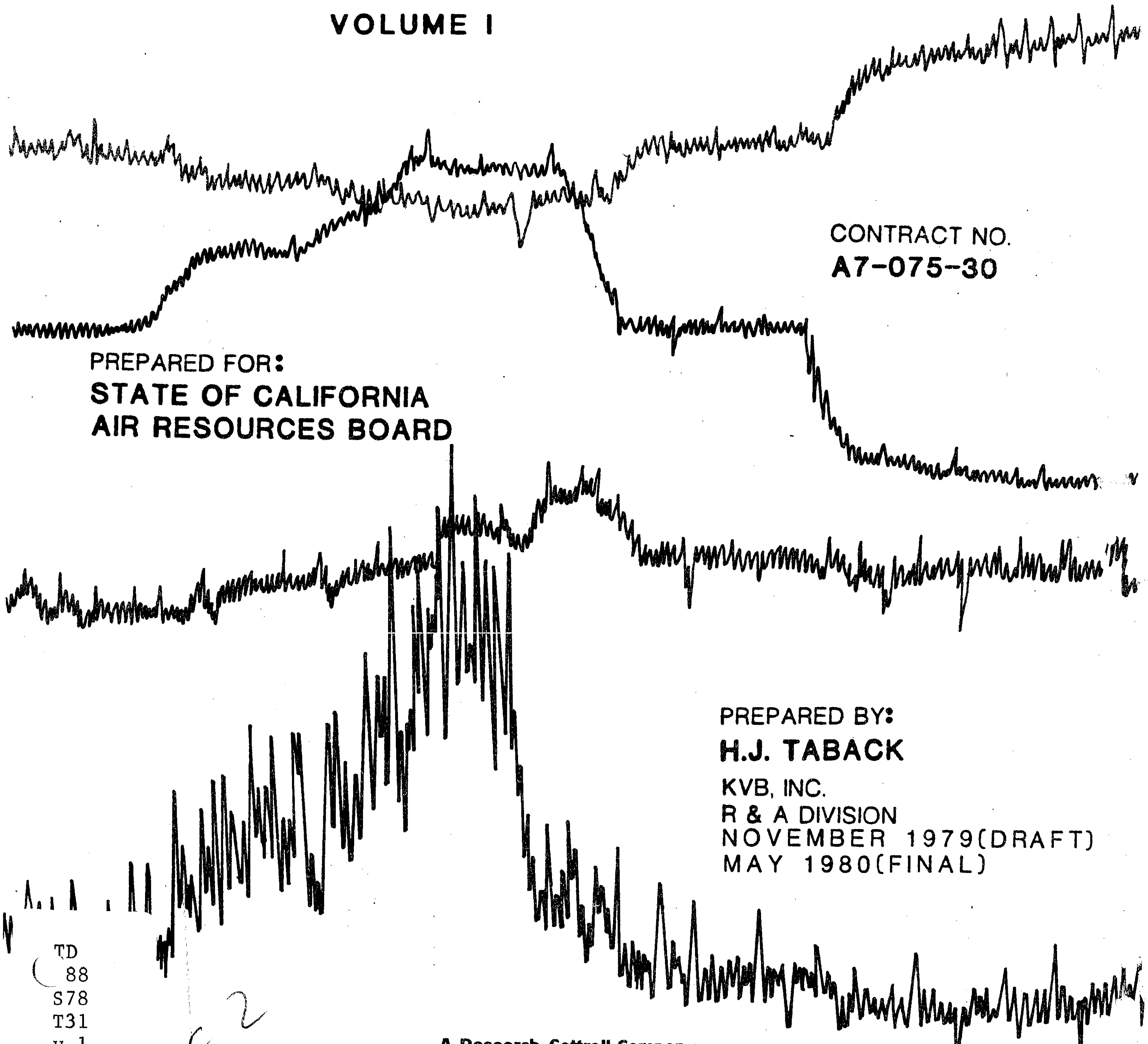
DETERMINATION OF AIR POLLUTANT EMISSION FACTORS FOR THERMAL TERTIARY OIL RECOVERY OPERATIONS IN CALIFORNIA

KVB 5807-842

FINAL REPORT
VOLUME I



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ABSTRACT

The purpose of this program was to determine the nature and extent of air pollutants resulting from thermally enhanced oil recovery methods in California and to determine emission factors for some of the sources of these pollutants.

Thermally enhanced oil recovery processes, also known as thermal tertiary oil recovery processes, employ techniques to heat viscous and entrapped subterranean oil so that it will more readily flow and can be pumped to the surface. Air pollution resulting from these processes occurs from essentially two sources, (1) the combustion of fuel on the surface to generate heating fluids which are injected into the well and (2) the release of contaminated steam from well vents, i.e.:

- steam generators, water heaters and air compressors which combust fossil fuels, and
- fugitive emissions emanating from the oil wells themselves at well vents and other equipment accessory to the wells.

The scope of the program included developing emission factors for particulates, sulfur oxides, nitrogen oxides, carbon monoxide and hydrocarbons, using both previously developed data and data from field tests conducted by KVB during the program.

In general, the emission factors developed in this report for steam generators are consistent with published EPA factors for industrial boilers, although some differences are noted. Differences in fuel composition at various locations and differences in combustion technology and equipment contribute to the variability of test results.

Well vent emissions were determined for two types of fields. In one field steam is generated on the surface and injected into the reservoir which is vented to the surface. This process is called steamflooding. In the other field, air is pumped into the reservoir where it is used to burn some of the crude in processes called in-situ combustion or fireflooding. This reservoir is also vented to the surface.

It was concluded that fireflooding appears to be less polluting than steamflooding, based on the few tests conducted on this program. It is strongly recommended that much more well vent data be obtained to substantiate the well vent emission factors developed on this limited-scope program.

Volume II of this report is an appendix that contains detailed data from tests conducted during the program.

ACKNOWLEDGEMENTS

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Mobil

Bill Dittman	District Production Superintendent
Jim Sklar	Operations Staff Engineer
Jack Burns	Line Supervisor
Marvin Cheeks	Unit Operator
Mitchell Lee	Engineer
John Klinge	Foreman

Tenneco

Hugh Swan	Senior Environmental Coordinator
Phil Hodder	Production Engineer
Leon Barry	Field Engineer
Don Shinn	Unit Operator

Santa Fe Energy Co. (CWOD)

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SECTION 1.0

INTRODUCTION AND SUMMARY

1.1 BACKGROUND

The increasing cost and diminishing supplies of domestic crude oil have made certain tertiary oil recovery techniques cost-effective where these techniques were previously not considered or utilized. These enhanced recovery procedures involve the stimulation of viscous or entrapped underground crude so that it may be pumped to the surface, hence recovered. This can be accomplished by the use of heat or chemicals such as surfactants or carbon dioxide. In this study only the thermally enhanced oil recovery (TEOR) techniques are considered because they have a significant impact on air pollution. In order to apply thermal stimulation to an oil reservoir, energy is required and in the conversion of fuel to heat energy, pollution is created. Throughout this report we will use the more commonly used terminology, TEOR, to mean "thermal tertiary oil recovery" as used in the program title.

In petroleum recovery there are three basic systems employed:

- Primary recovery, using only naturally occurring forces or mechanical pumping methods.
- Secondary recovery, resulting from injection of water or natural gas into a petroleum reservoir.
- Tertiary recovery (enhanced recovery) using processes beyond that economically recoverable by conventional primary and secondary methods.

This report addresses two TEOR techniques:

- Steamflooding, the injection of steam into an ejection well and the consequential oil production from nearby wells. (A modification of this process is sometimes called steam stimulation or "Huff & Puff" which is the periodic injection of steam into a well followed by the production of oil from the same well.)

- In-situ combustion, more commonly called fireflooding, the injection of air into a reservoir to burn part of the oil in the reservoir to generate heat to stimulate oil flow from nearby wells.

Much of the naturally occurring crude oil in Central and Southern California is generally a high viscosity, high density, tar-like substance. Since 1963 oil producers have injected steam into these wells to improve recovery. In fact, most of the TEOR operations in the country are located in California concentrated primarily in Kern and Monterey Counties. The emissions from the oil field steam generators, primarily in Kern County, have contributed to an air pollution problem in the San Joaquin (or Central) Valley. The Valley is a major national agricultural zone upon which pollution could cause incalculable crop damage. To compound the problem, the Central Valley is undergoing a population increase (Ref. 1) whereby excessive air pollution to a large population may be intolerable. The meteorological conditions of the Central Valley are not unlike those of the South Coast Air Basin where frequent conditions of stagnation and poor ventilation result in the build-up and long residence time of air pollutants.

The steam generators used in the oil fields are very different from industrial boilers. In most cases the fuel used is the crude oil produced at the site. In California, this crude oil contains one to two percent sulfur and is relatively high in trace metals. This is the primary fireside difference between oil field steam generators and industrial boilers of comparable size. While the EPA has documented industrial boiler emission factors in their publication, AP-42 (Ref. 2), there was concern that the emission factors for oil field steam generators fired with lease crude would be different than those in AP-42. Furthermore, there was interest in characterizing the trace metals content in the particulate emissions.

Relatively little reliable information was available on emissions from oil well vents. The Kern County Air Pollution Control District had some data on some tests run in a Getty Oil field. The validity of that data was questionable since the hydrocarbon emission rates reported were of the same order of magnitude as the crude production for the field.

1.2 OBJECTIVE

The principal objective of this program was to investigate the emissions associated with TEOR operations and develop emission factors for nitrogen oxides, sulfur oxides, particulate matter (including trace metals), carbon monoxide, hydrocarbons and hydrogen sulfide. These emission factors were to be developed as a function of the crude oil production rate (lb/bbl produced). For the steam generators, emission factors as a function of fuel consumption (lb/1000 gal crude burned) were to be developed to compare with those in AP-42 (Ref. 2).

Secondary objectives were to investigate control technology and to predict the potential increase in pollution as the result of growth.

1.3 BUDGET

The extent of the research funds expended toward meeting these objectives was the equilvalent of one engineering man year which included all investigative work in the literature and with government agencies and oil companies; coordination with the Western Oil and Gas Association (WOGA) to arrange for test sites, review results, etc.; field test operations; analyses work; supervision and reporting.

1.4 APPROACH

This program was designed to collect available emissions data on TEOR operations in Kern and Monterey Counties and to conduct selected field tests within budgetary constraints to verify the existing data and generate new emission data especially in the area of well vent emissions.

KVB collected TEOR emissions test data from Kern and Monterey Counties pollution control authorities, oil producers, the California Air Resources Board and from earlier KVB field studies. These data included emissions of particulates, sulfur dioxide (SO_2), carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x), as well as other pertinent and related information such as fuel composition, equipment types and configurations, and methods of operation. KVB further gathered current information on production figures, equipment inventories, predicted future operations, and sorted and compiled these data into appropriate tables and diagrams to facilitate assimilation by the reader.

KVB conducted field studies to determine the nature and extent of emissions caused by the prevalent TEOR techniques. Two field studies were conducted to determine the emissions from oil field steam generators. In addition, two field studies were conducted to determine emissions escaping from well vents as a consequence of steam injection and in-situ combustion.

From the data gathered, emission factors were generated on a lb/bbl-crude-produced basis for both steam and fireflooding processes as well as on a lb/1000 gal-crude-burned basis for the steam generators. X-ray fluorescent analyses of the particulate catch provided information on the percent composition of trace elements. These data are presented in Section 4.0. A summary of these data appeared in a paper delivered at the Air Pollution Control Association's 1979 annual meeting in Cincinnati, OH (Ref. 3). Detailed test data and other supporting information are presented in a separate volume as an appendix to this report.

Finally, some brief analyses of generator test data, field observations and previous work was used to discuss control options and make some projections of future emissions.

1.5 FINDINGS

KVB developed emission factors for major pollutants from the literature survey and for the current field tests. For the steam generators alone, the emission factors as a function of crude oil burned are:

Pollutant	lb/1000 gal
TSP	
Solid	8S*+3
Total**	23
SO_x As (SO_2)	155 S*
CO	5.8
HC (Non-Condensible)**	1
NO_x	51

*S = Percentage sulfur in fuel oil.
**TEOR steam generators in normal operating condition emit no condensible hydrocarbons.

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For the two different types of TEOR as a function of the barrels of oil produced (gross; i.e. including oil burned as fuel in the steam generation) the emission factors are:

Pollutant	lb/bbl Produced*	
	Steamflood	Fireflood
TSP (Total)	0.43	0.15
(Condensible HC)	(0.09)	(0.15)
HC (Non-Condensible)	0.0054	0.25
Total HC (Cond. & Non Cond.)	0.095	0.40
SO_x as SO_2	1.7 S	0.03
CO	0.076	0.009
NO_x as NO_2	0.43	0.05
H_2S	0.0003	0.03

We then applied these emission factors to present and future predicted oil recovery operations in order to predict the magnitude of uncontrolled pollution resulting from TEOR operations and found the following to be the emissions of Kern and Monterey Counties operations during 1977 and 1978:

	Emissions, tons/day		
	Kern	Monterey	Total
• Particulates (excluding condensible H/C)	69	5	74
• SO_x** as SO_2 (assuming 1.2% avg. fuel sulfur)	260	20	280
• CO	11	1	12
• Hydrocarbon (including condensible H/C)	28	2	30
• Nitrogen oxides as NO_2	65	5	70

The emissions tabulated above are based on a gross production rate for 1977-78 of 230,000 bbl/day. Since 1978 the TEOR production has increased. Indications are that it will double by 1983 to 1985 and will continue to rise through the end of the century. The Congressional Office of Technology Assessment

*These data are based on very few tests and should be treated as a qualitative indications of emission. When fuel consumption data are available, the emissions from oil field steam generators should be calculated from emission factors on the previous page.

**Assuming zero control, although some units are controlled. With existing controls these emissions are estimated at 500 tons/day.

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estimates that six-billion barrels of TEOR crude will be produced primarily in California by the year 2000, which is equivalent to an average daily production rate of over 700,000 barrels. Because of extensive emission controls now required on these sources, it is difficult to predict the future emissions. An investigation of this aspect is beyond the scope of the current contract.

An X-ray fluorescence (XRF) analysis of particulate samples from steam generators and well vents indicate that the permanent trace elements emitted from the few TEOR sources tested were iron (from underground piping), nickel and vanadium (from the crude oil burner), plus chlorine and calcium (from the connate water produced with the crude oil). XRF does not detect low atomic number elements which include sodium, silicon, lithium and beryllium.

KVB found in the course of testing and reviewing previous tests of steam generators that NO_x and CO and unburned hydrocarbon emission reductions can be achieved by combustion optimization and maintenance procedures. Further NO_x emission reductions (i.e. beyond those from combustion optimization) can be made by use of ammonia injections both with and without the use of a catalyst. Particulate and SO_2 emissions from steam generators may also be reduced by conventional scrubbing techniques but require the addition of control equipment. There are some emerging control techniques involving the injection of dry chemicals and slurries and the collection of residues in a baghouse, which hold great promise for a combined system to control both SO_x and particulate emissions.

Well vent emissions are less defined and more testing is needed. In the recent field tests, well vent emissions were generally low and consisted mainly of hydrocarbons for which control techniques are well established.

Fireflooding recovery procedures yield much lower over-all pollution, except for hydrocarbons which can be controlled. The economics of fireflooding plus the fact that many reservoirs do not lend themselves to this technique make it difficult to assess its over-all potential and usefulness.

The U.S. Department of Energy (DOE), through the Sandia Corporation, is developing a compact steam generator that can be lowered to the bottom of an injection well where it will be fed fuel, air and water and will produce steam to drive crude oil toward surrounding production wells. The object of this project, called "Deep Steam," is to get steam to very deep wells where much of the steam's energy would be lost to the strata if it were injected from the surface. A secondary benefit, however, is that this submerged generator's combustion products are injected into the well which may act as a natural scrubber and reduce atmospheric emissions.

1.6 CONCLUSIONS

- Steam generator operation can be improved to lower NO_x emissions by combustion modifications. More extensive reductions are possible by ammonia injection techniques.

- Simple water scrubbers have been installed on steam generator stacks which appear to reduce SO_2 emissions approximately 80% on the basis of one test. Greater reductions may be possible by use of other flue gas desulfurization techniques.

- Particulate emissions can be lowered by the installation of add-on control devices such as a precipitator or baghouse. The simple water scrubbers, used in San Ardo for SO_2 reduction, also appear to reduce particulate emissions approximately 50% on the basis of one test.

- Fireflooding TEOR seems to produce much less pollution based on the few tests conducted on this program.

- Further emission tests on well vents, both from steamflooding and fireflooding operations should be performed to ascertain the nature and extent of pollution arising therefrom.

- DOE's program to develop a down-well steam generator should be followed because of its potential for reduced pollution aside from its potential to improve energy efficiency.

SECTION 2.0

TEST SITES AND CALENDAR

The two tertiary methods under consideration and test in this program are steamflooding and fireflooding.

Steamflooding consists of generating large quantities of steam in a surface boiler and injecting the steam into oil wells. The steam heats the oil bearing strata causing the oil to flow to the pumps. As the steam cools, some of it condenses and the remainder returns to the surface at the various production wells where it is vented to the atmosphere carrying pollutant emissions aloft or vented to a hydrocarbon recovery unit where the hydrocarbon vapors are condensed and recovered. Variations in this process include continuous steam injection or intermittent or cyclic steam injection.

Most commonly, the steam generators burn crude oil produced at the well site, this being the most convenient and least expensive steam generating fuel. Steam generators will therefore emit NO_x, CO, SO_x, particulates and small amounts of hydrocarbons during the combustion (steam generating) process. At the same time emissions occur from well vents. These emissions are primarily water vapor containing hydrocarbons, particulates and in lesser quantities hydrogen sulfide and mercaptans. These latter sulfur emissions will vary considerably according to the location of the specific oil field.

In fireflooding, air is injected into the reservoir using compressors usually driven by natural gas fired, reciprocating engines. The in situ gas and oil plus the injected air are ignited generating heat and steam. Emissions from this TEOR method include the compressor engine exhaust plus the well vent emissions which are essentially the same as those from the steamflooding method since the steam generated underground is vented to the surface. A stylized illustration of the fireflooding process is presented in Figure 2-1.

The locations selected for steamflooding testing in this program were:

Mobil Oil Company's San Ardo field, Monterey County, CA, Steam Generator Unit No. 22-5 tested July 19 and 20, 1977;

Tenneco Oil Company's Kendon field, Kern County, CA, Steam Generator Unit No. 43, tested July 21, 24, 25 and 26, 1977.

The Mobil and Tenneco units were tested for particulates, SO_2, NO_x, hydrocarbons and trace metals.

Another steamflooding operation was tested for well vent emissions only. The site tested is:

Chanslor-Western Oil and Development Company (CWOD)* Midway Sunset Field, Kern County, CA, Unit No. 42, tested July 27, 1978.

The well vent emissions measured were particulates, hydrocarbons, hydrogen sulfide and trace metals.

Tests of fireflooding operations were performed at Mobil Company's Lost Hills field, Kern County, CA on August 24 through 26, 1978. Well vent emissions were tested for particulates, trace metals, SO_2, CO, NO_x, H_2S and hydrocarbons. At the Lost Hills operation, Mobil uses five injection stations to flood 40 production wells. We sampled the vents on five of these wells. The compressor emissions were not measured because the emission factors for large internal combustion engines are well documented in the EPA's document AP-42 (Ref. 2). From time to time, this process uses a portable steam generator of 10^6 Btu/hr in size to clean out the inlet and vent lines. We were told that this apparatus is only used approximately 10 days per year at this site. Therefore, these emissions were ignored.

Figure 2-2 shows the locations of TEOR operations in California and locates the specific test sites used on this program.

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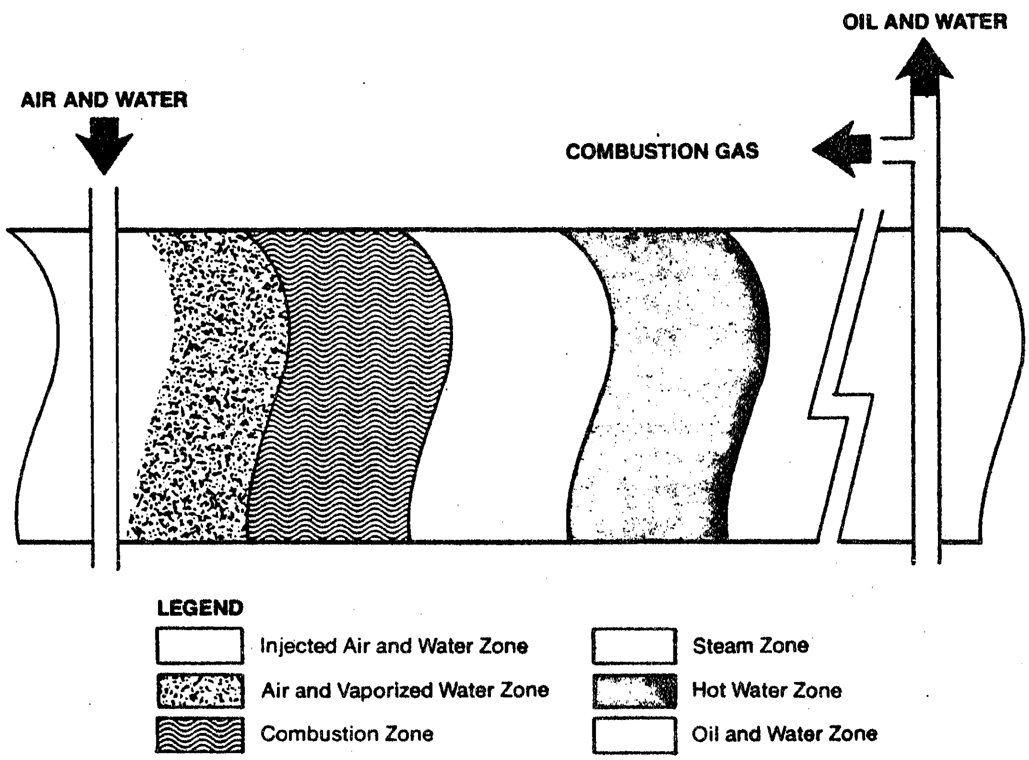
* Chanslor Western Oil and Development Company (CWOD) recently became Santa Fe Energy Company. In this report, they will be referred to as the more familiar "CWOD."



*Illustrations redrawn and printed with permission of the National Petroleum Council. © National Petroleum Council, 1976.

Figure 2-1. Fireflooding process. (Ref.4)

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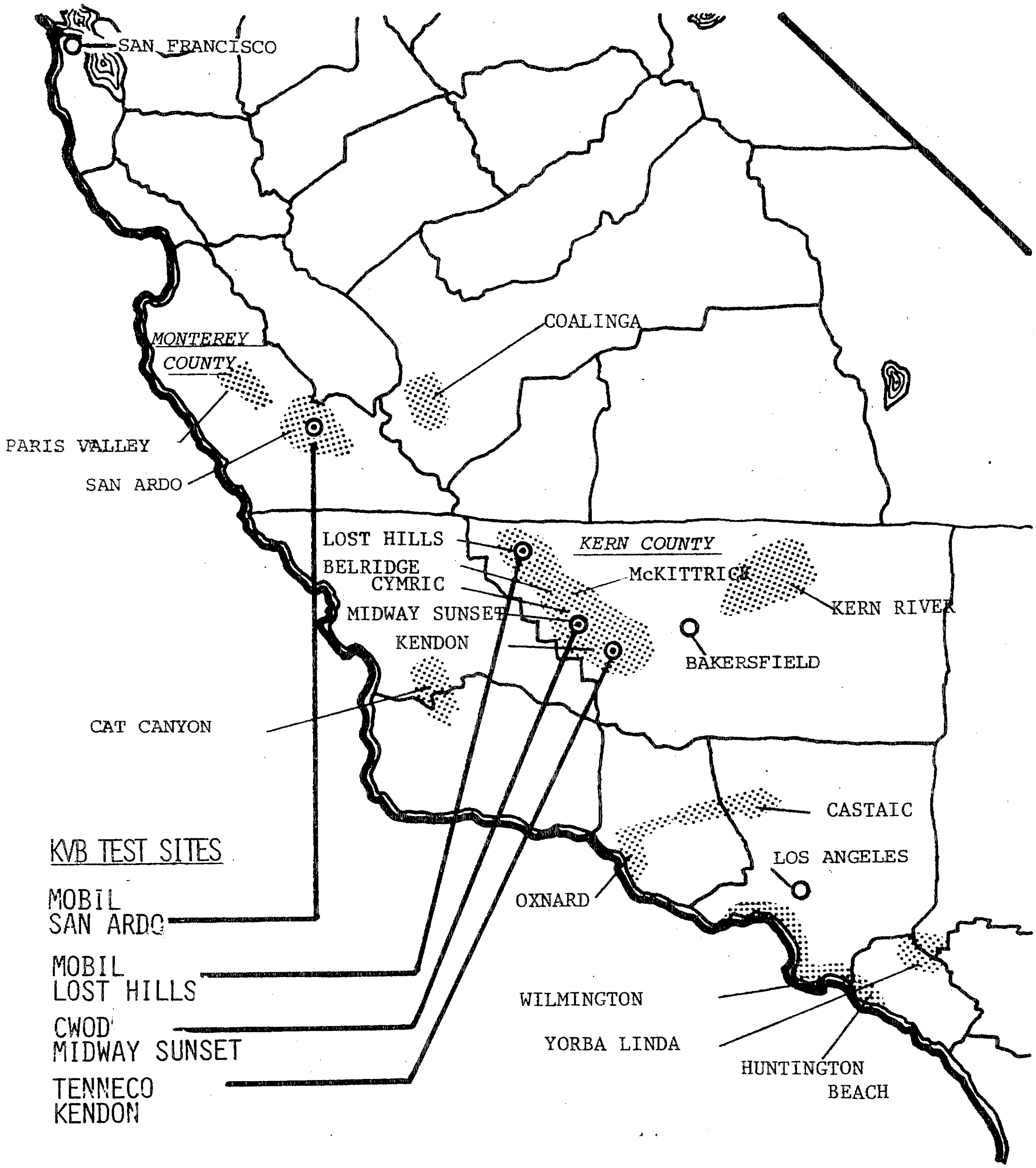

Figure 2-2. TEOR operation sites in California showing location of KVB tests.

SECTION 3.0

TEST OPERATIONS

3.1 MOBIL SAN ARDO STEAM GENERATOR

The Mobil Oil Company's San Ardo Field Steam Generator No. 22-5 is a CE NATO 50×10^6 BTU/hr steam generator equipped with an economizer,* a North American burner and a Mustang Engineering SO_2 scrubber. Fluegas samples were taken at the scrubber inlet and outlet. Adequate platforms and access were available for the required testing of this unit. Schematic diagrams of the generating unit and appurtenances including test sites are displayed in Figure 3-1. Photographs of the unit are presented in Figures 3-2 and 3-3.

As the SO_x scrubbing medium the system uses connate water produced from the oil well along with the crude oil and separated from the oil in a heat treater dewatering system.

The steam generating unit was tested at four excess oxygen levels: approximately 4% (normal operation), 1%, 3%, and 6% with samples taken as diagrammatically depicted in Figure 3-4.

SO_x, NO_x, CO, HC samples were taken at all four excess O_2 levels. EPA Method 8 SO_x, Method 7 NO_x, and total particulates by Method 5 were taken at normal (4%) excess oxygen levels across the scrubber.

Duplicate hydrocarbon samples were taken at each oxygen level plus ambient background hydrocarbon samples. Fuel samples were taken daily near the burner inlet. Fuel scrubber water samples were taken at the supply tank outlet and scrubber outlet.

Some difficulties owing to producer equipment problems were encountered during operations in holding excess oxygen levels at steady state conditions

* An economizer is a set of steam generating tubes added to the basic boiler to recover additional heat from the combustion gases.

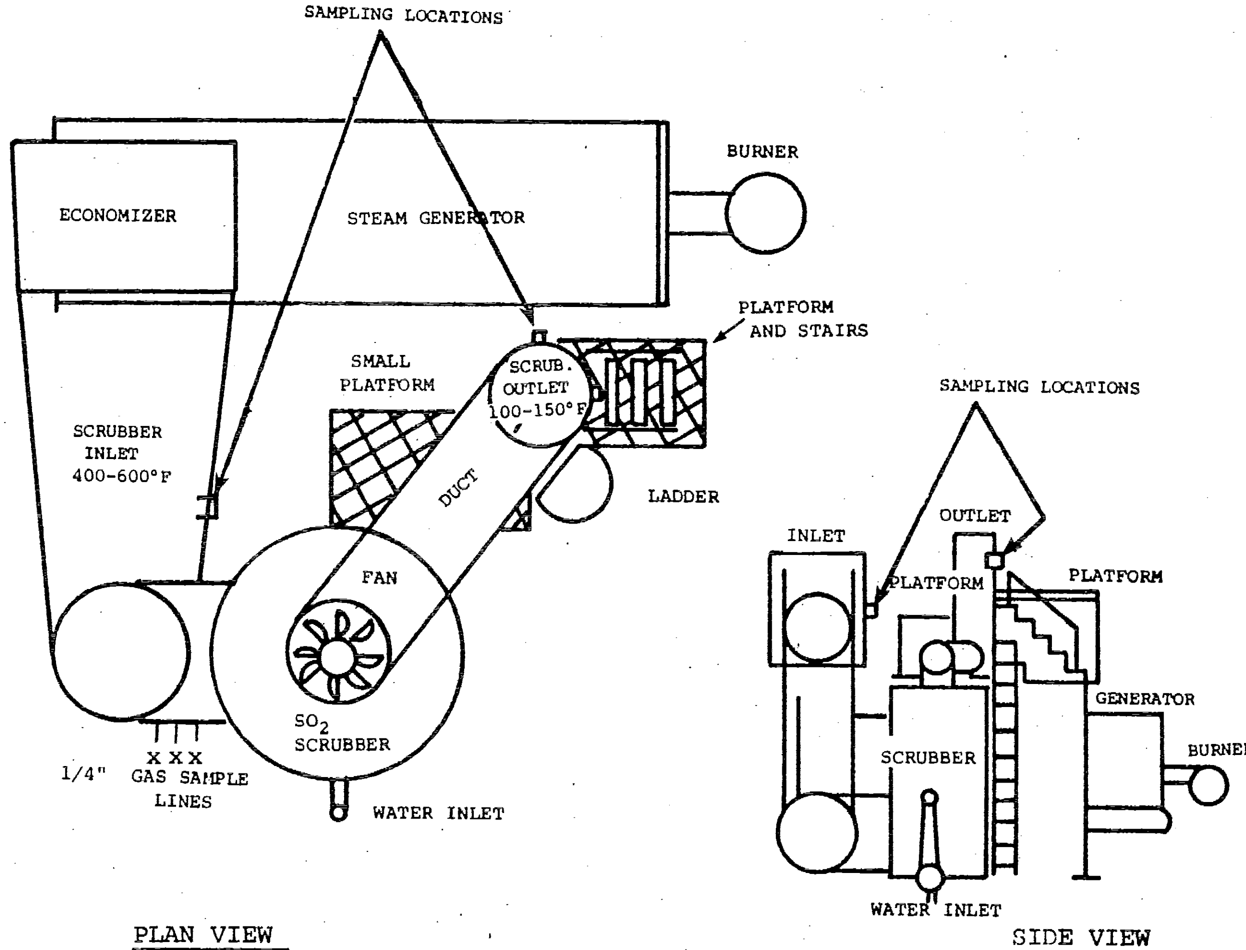

Figure 3-1. Mobil San Ardo - CE Natco 50mm Btu steam generator with Mustang Engineering SO_2 scrubber showing sampling locations.

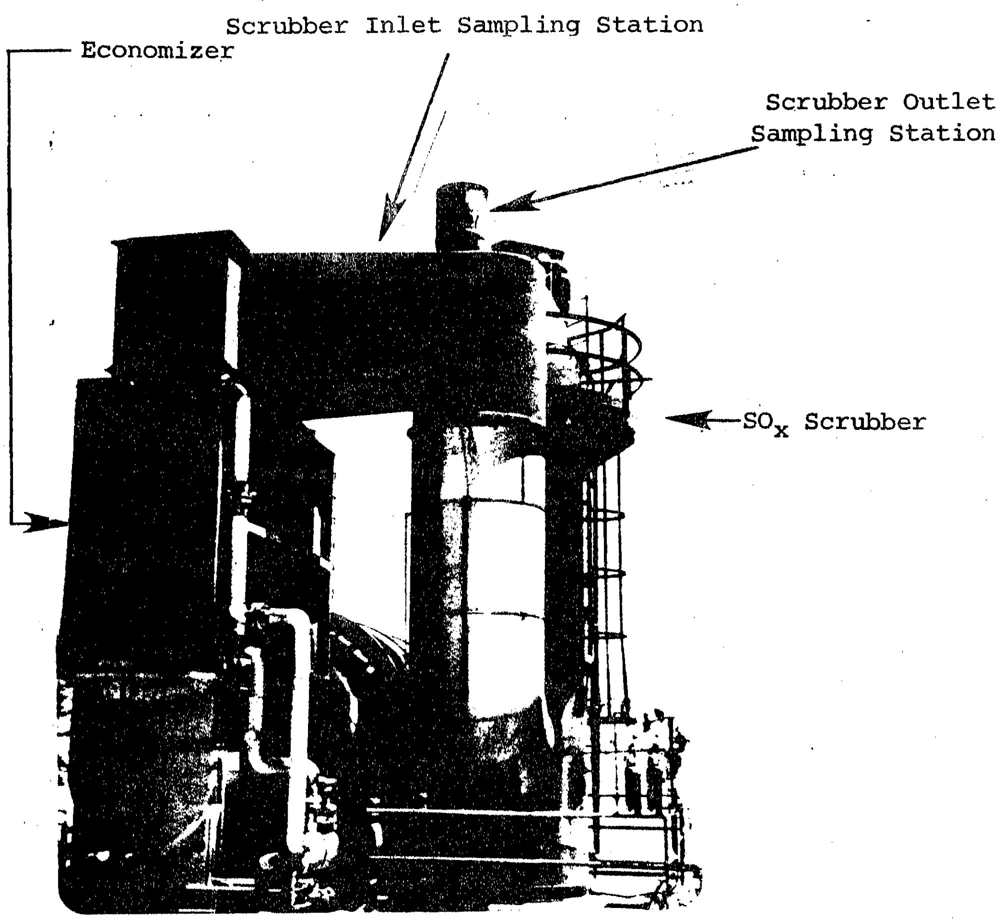

Figure 3-2. TEOR steam generator at Mobil San Ardo, showing various components and scrubber inlet sampling system.

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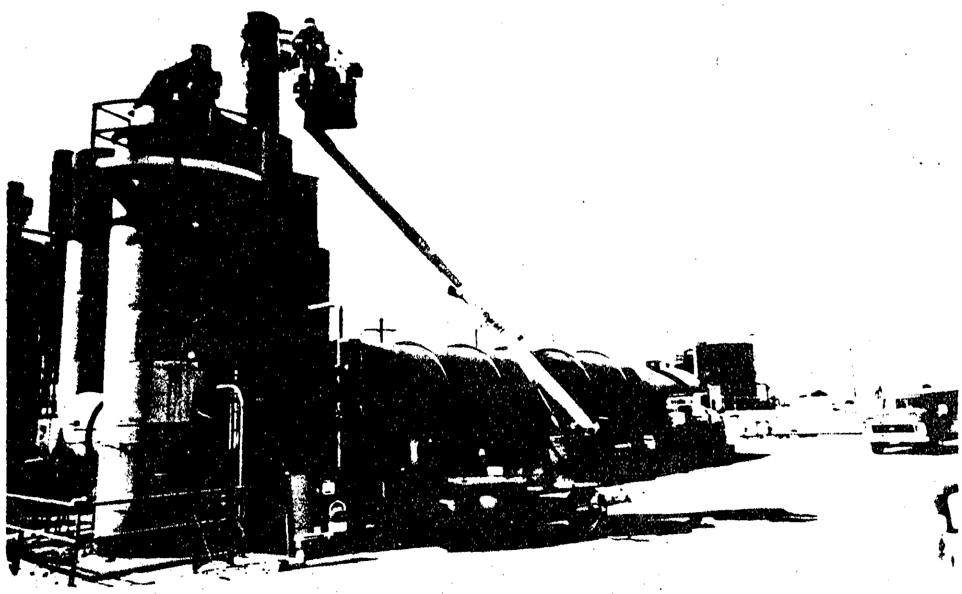

Figure 3-3. 50 million Btu/hr TEOR steam generator at Mobil San Ardo with SO_2 scrubber in foreground showing test crew sampling scrubber outlet.

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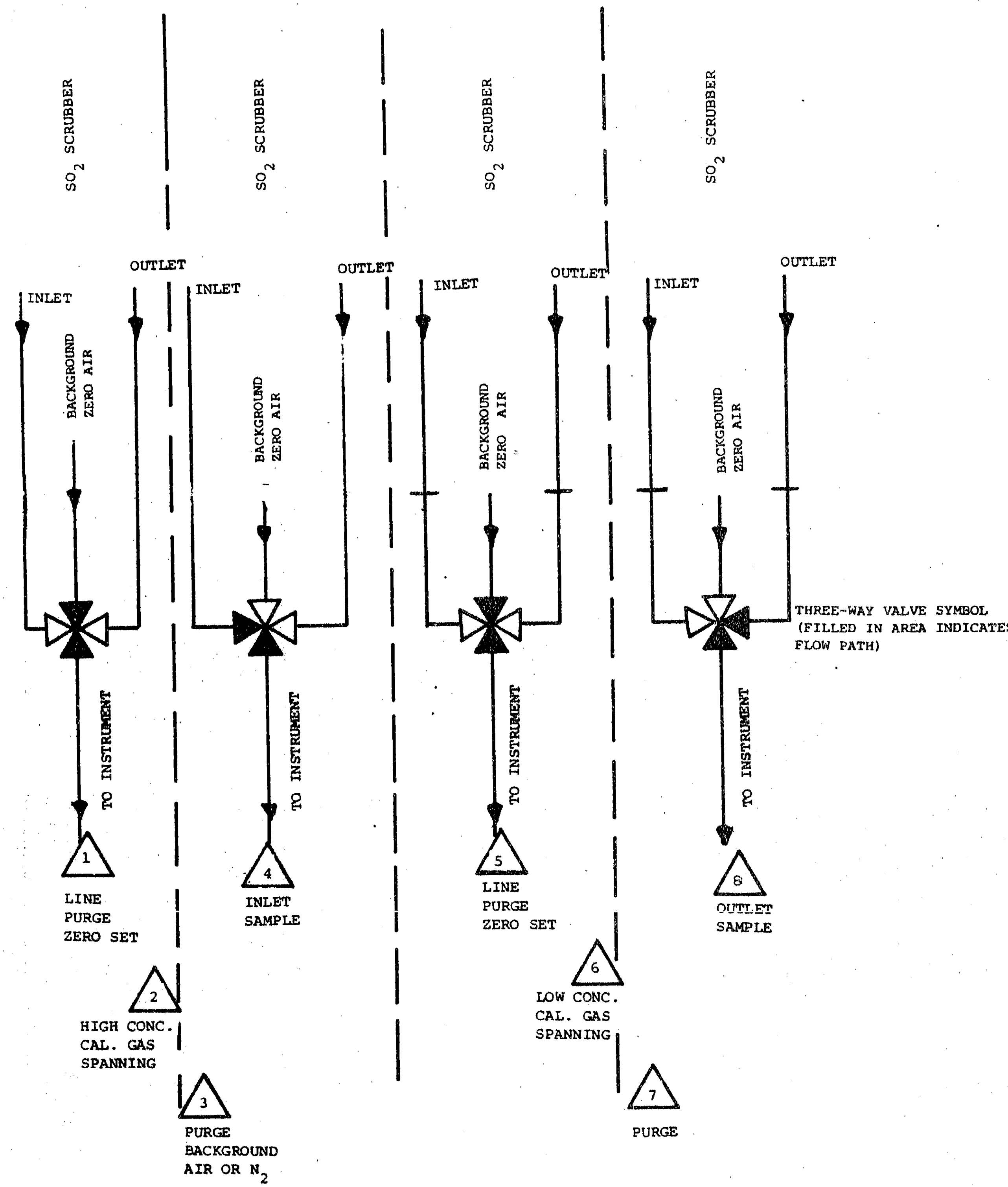


Figure 3-4. Dual sampling mode of Mobil San Ardo tests.

at the various excess oxygen target levels. The problem is attributed to foam in the crude oil fuel supply.

Reservoir steam injection data and oil production data related to these tests were provided by the Mobil Corporation and may be found in the Appendix.

3.2 TENNECO KENDON STEAM GENERATOR

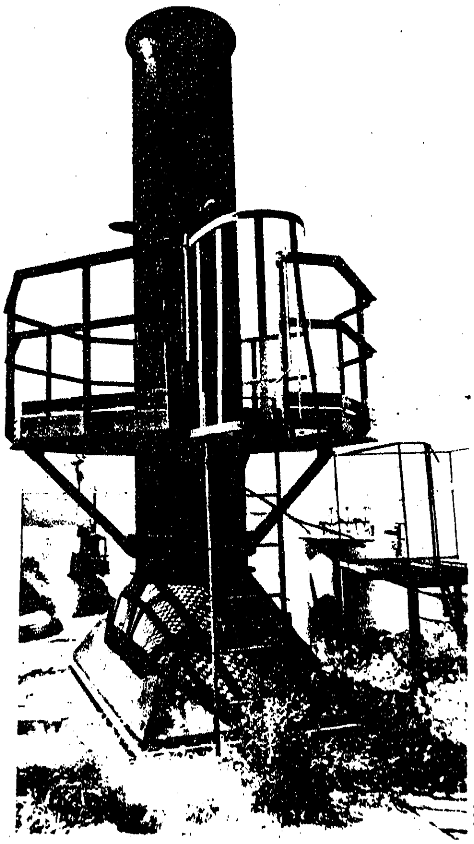
The unit tested at the Tenneco Kendon lease is a Thermotics $50X10^6$ Btu/hr steam generator (No. 43) equipped with an economizer and a North American burner. No emission controls were installed. The unit was fitted with the special emissions sampling stack pictured in Figure 3-5. A close-up of the steam generator in its normal condition without the sampling stack is shown in Figure 3-6. Note that the combustion gases are exhausted from an opening at the top of the economizer. Figure 3-7 is a picture of the steam generator with the stack in place and the KVB mobile laboratory parked beside the unit sampling the emissions. Fluegas samples were taken at four excess oxygen levels: approximately 4% (normal operation), 2%, 3%, and 5%.

Fuel samples were taken daily during operations. Reservoir steam injection and oil production data related to these tests were provided by Tenneco and may be found in the Appendix.

3.3 CWOD STEAMFLOOD VENT TESTS

CWOD Midway Sunset Field Unit No. 42 was tested for both condensible and non-condensible well vent emissions. Schematic diagrams of these systems are depicted in Figures 3-8 and 3-9.

The flow rate at the well head (Fig. 3-8) was measured by channeling all of the emissions through an impinger train and then to a gas meter at the end of the train. The steam had sufficient pressure to feed the train so that no pump was required. The volumetric flow rate was calculated from the volume of liquid collected in the impingers and the volume of gas recorded by the meter.



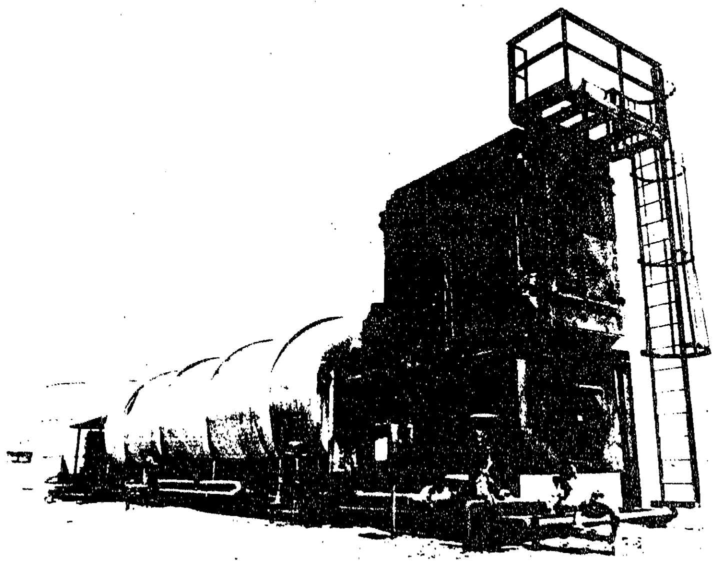


Figure 3-6. Thermotics 50 MM Btu/hr steam generator at Tenneco Kendon lease.

Figure 3-5. Special source emission sampling stack for Thermotic 50 MM Btu/hr steam generator at Tenneco Kendon.

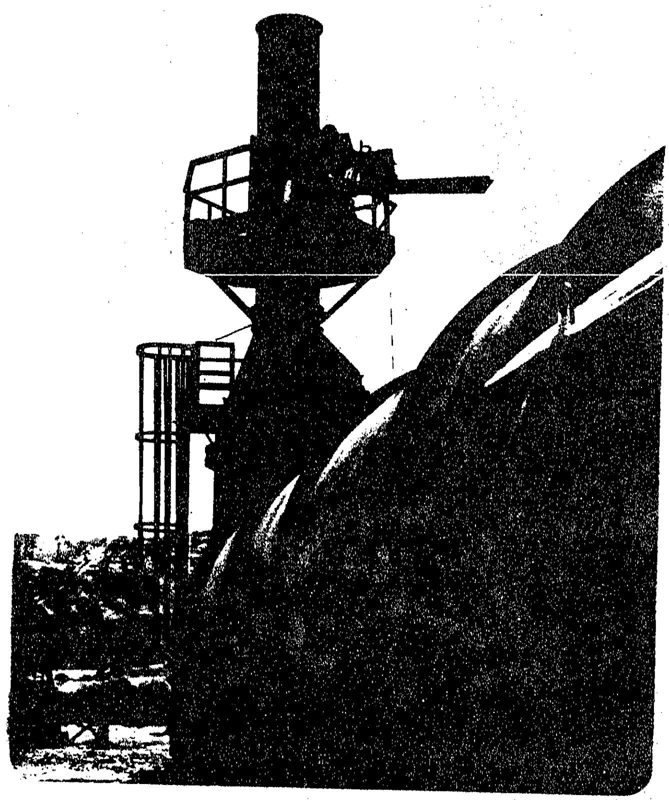
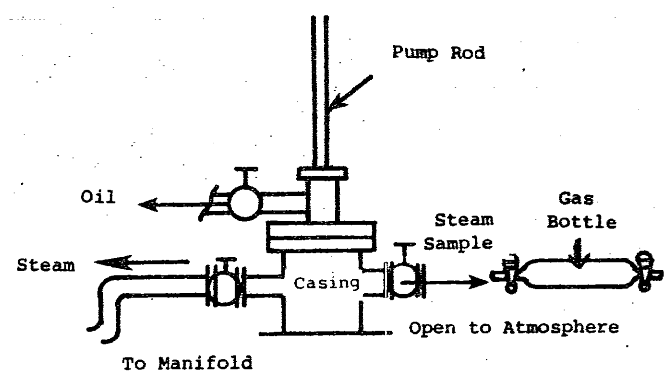
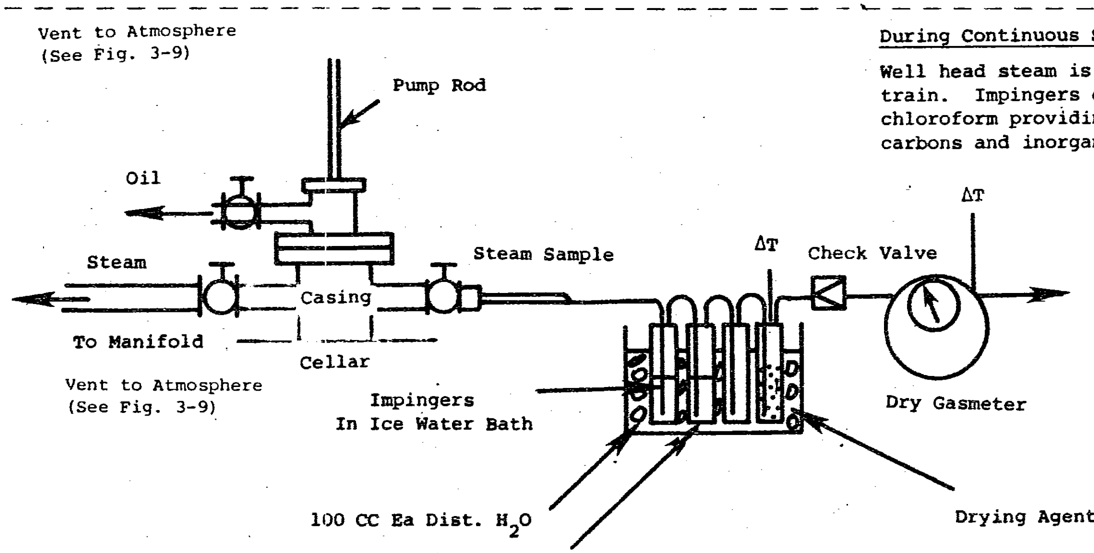


Figure 3-7. Testing of steam generator at Tenneco Kendon showing stack in place.



During Grab Sampling

Well head steam is vented through a 250 ml double ended glass container. Container is purged 10 minutes and then sealed. Sample is analyzed by gas chromatography for non-condensible hydrocarbons and H_2S.



During Continuous Sampling

Well head steam is vented through sample train. Impingers extracted with methyl chloroform providing condensible hydrocarbons and inorganic fraction analyses.

Figure 3-8. CWOD well head emissions test - schematic diagrams.

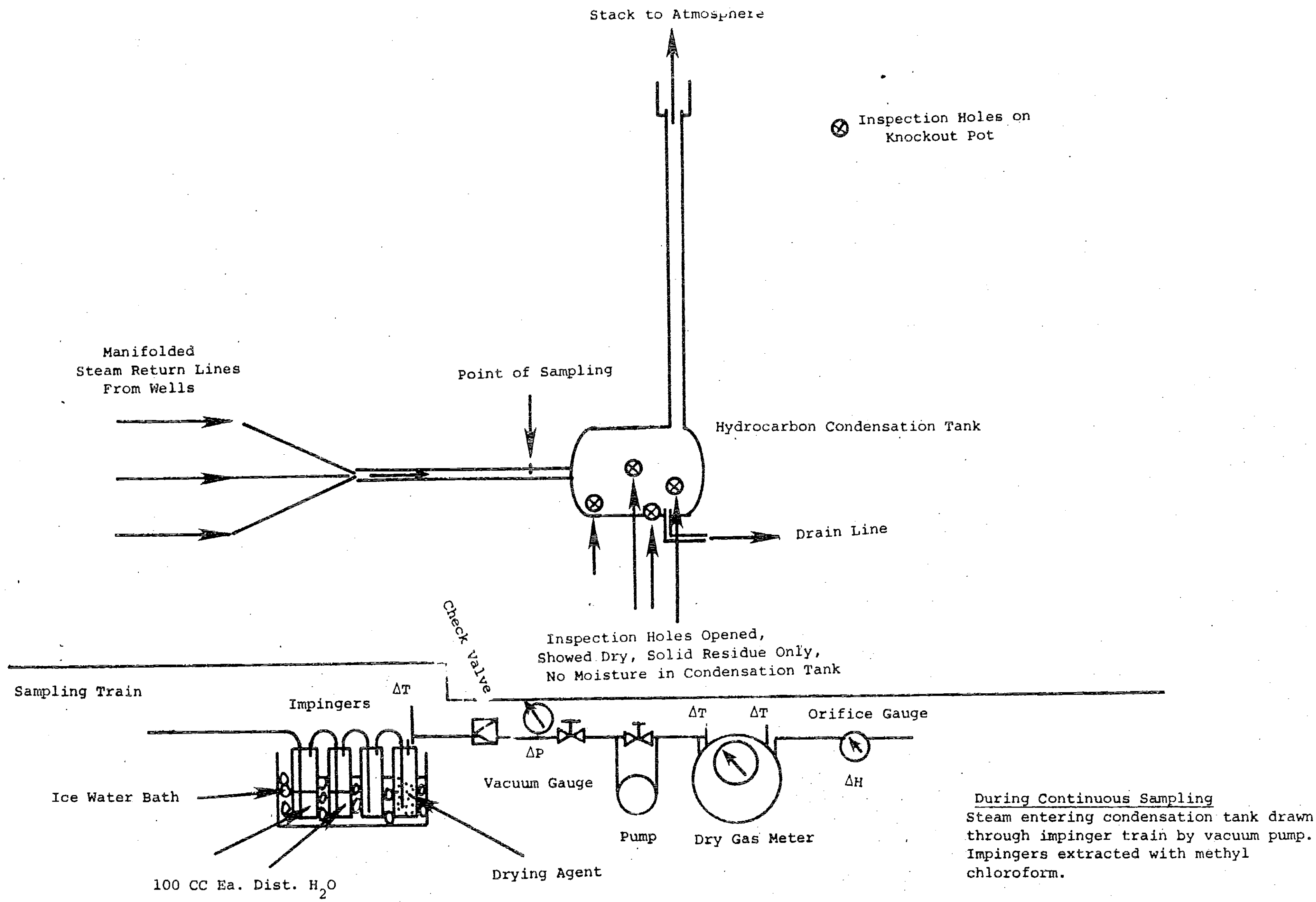


Figure 3-9. CWOD well vent emissions test - schematic diagram of sampling at hydrocarbon condensation tank.

The well system under test was constructed so that the steam return lines from the stimulated wells were brought together in a single manifold, then to a hydrocarbon condensation tank and vented to the atmosphere as shown in Figure 3-9. Our sample train of impingers, gas meter, etc., was located to sample on the manifold return line before the condensation tank. The condensation tank is equipped with inspection holes, which upon examination revealed no moisture. Only a dry residue was present. It appeared that this condensation tank was not functioning to reduce hydrocarbon emissions.

CWOD supplied KVB with test data for its $50X10^6$ Btu/hr steam generator located at this site. The test data were developed during 1977 and are comparable to the KVB test data obtained at Mobil and Tenneco during this program. CWOD also supplied reservoir steam injection and oil production data relevant to the KVB emission tests.

3.4 MOBIL LOST HILLS FIREFLOOD VENT TESTS

This operation involves three air compressors powered by natural gas fueled reciprocating engines. One compressor is rated at 350 H.P delivering one million cubic feet per day. The other two compressors were rated at 600 H.P. each delivering two million cubic feet of air per day.

As previously noted, the air is injected through five wells to the reservoir which supplies 40 production wells. Each production well has a vent pipe between 2 and 4 inches in diameter and is 10 to 20 feet high. Figure 3-10 depicts the field under study. We selected five wells, Nos. 302, 304, 308, 317, and 344, for sampling which approximated a diagonal through the field. The sampling setup was identical to the wellhead sampling performed at CWOD Midway Sunset shown in Figure 3-8.

3.5 TEST METHODS AND QUALITY CONTROL PROCEDURES

Table 3-1 lists the principal test methods employed during the field testing operations in this program. Generally the standard EPA methods were employed where available. On the well vents, because the emissions are largely steam, it was not possible to use a Method 5 train which incorporates a filter upstream of the impinger. The steam would immediately clog the filter with water. Therefore, a modified SCAQMD train, essentially the Method 5 train with the filter removed, was used on the vents.

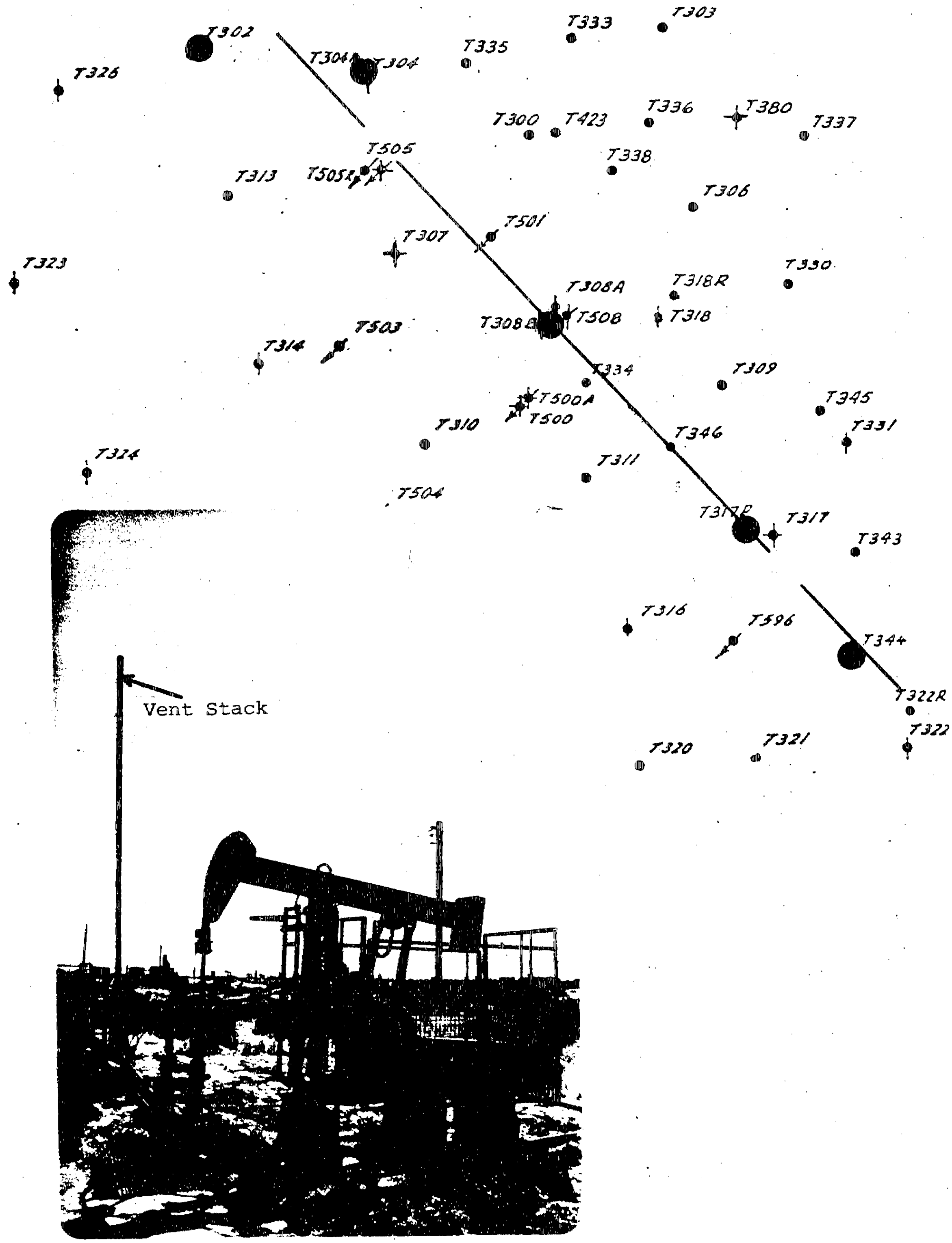


Figure 3-10. Mobil Lost Hills fireflooding TEOR field showing location of five wells tested marked (●) relative to the other wells in the field and picturing a typical well head with a vent stack.

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TABLE 3-1. TEST METHODS

Test Item	Method
Mass Flow	EPA Methods 1-4
Particulates	EPA Method 5,* Modified SCAQMD (on well vent)*
$SO2 - SO_3$	EPA Method 8
NO_x	EPA Method 7
Hydrocarbons	G.C. Analysis of grab samples taken in evacuated borosilicate glass tubes
Trace Metals	X-ray fluorescence using the inorganic fractions of the impingers catch of the particulates train.

* On both Method 5 and the SCAQMD method, the impinger catch was extracted with methyl chloroform to obtain a condensible organic fraction as well as an inorganic fraction.

Instrumentation employed in the KVB field laboratory van was as follows:

TABLE 3-2. INSTRUMENTATION

Test Item	Instrument
SO_2	DuPont photometric analyzer calibrated with zero and 971 ppm span gas
NO_x	TECO chemiluminescence calibrated with zero and 417 ppm NO span gas
CO_2, CO	Horiba non-dispersive infrared calibrated with zero air and 12.95 volume percent CO_2 and 250 ppm CO span gas
O_2	Teledyne polarographic calibrated with zero N_2 and 4 volume percent oxygen span gas

Quality control on instrumentation was maintained as follows: All calibration gases were certified to National Bureau of Standards analyzed gases. Zero and span checks were made on all instruments not less than three times each test day, i.e., before each test, during the field test and at the conclusion of a field test. Span and zeros varied little and were reset according to needs each time. Methods 7 and 8 wet chemistry determinations were used as primary references for NO_x and SO_2 tests respectively.

Stringent quality control measures were maintained on continuous reading analyzers during the testing of steam generating equipment. Analog output was recorded at 10 cm/hr and 5 readings were integrated in each cm. Each cm. integrated was corrected for zero and span using the primary reference data and the daily calibration factors were incorporated into regression analyses. Each test set was based on not less than 30 integrated data points. The maximum acceptable standard deviation was ± 10%. Span correction factors used in data development were as follows:

TABLE 3-3. LEAST SQUARES CALIBRATION EQUATIONS*

PARAMETER	MOBIL, 7-19-78	SAN ARDO 7-20-78	TENNECO, 7-25-78	KENDON 7-16-78	CAL GAS
NO cold line	Y=(1X)+0,	Y=(1X)+0	Y=(1X)+3	Y=(.93X)+3.2	417 ppm
NO hot line	Y=(.91X)+.7,	Y=(1X)+0	Y=(.90X)+3	Y=(.90X)+3	417 ppm
NO_x hot line	Y=(.90X)+7,	Y=(1X)+0	Y=(1X)+0,	Y=(.93X)+3.2	423 ppm
SO_2 cold line	Y=(1X)+0,	Y=(1.05X)+0	Y=(1X)+0,	Y=(1X)+0	971 ppm
SO_2 hot line	Y=(1X)+0,	Y=(1.05X)+0	Y=(1X)+0,	Y=(1X+0)	971 ppm
O_2 hot line	Y=(1X)+0.1,	Y=(.90X)+0	Y=(.99X)+0,	Y=(1.01X)+0	4%
CO_2 cold line	Y=(1.03X)+0,	Y=(1.03X)+0	Y=(1.0X)-0.08,	Y=(1.05X)-0.08	12.95%
CO cold line	Y=(1X)+30,	Y=(1X)+50	Y=(.99X)-2,	Y=(1.04X)-2	250 ppm

X = Chart reading
Y = Pollutant concentration, PPM

We anticipated that in the course of testing the CWOD Midway Sunset and Mobil Lost Hills sites for well vent emissions, we would need to employ "trace methods" analysis procedures. The methods we used are especially adaptable to low concentrations, static situations or where stream flows are very small. The trace test method employed was Draeger Detector tubes (Ref. 5).

Draeger Detector tubes were used for measuring H_2S, SO_2, NO_x, CO, H_2O, CO_2, and HCN concentrations. A performance evaluation of Draeger Detector tubes (Ref. 5) is in Table 3-4 below.

TABLE 3-4. DRAEGER TUBE ERROR ESTIMATE

Draeger Tube	Certified Coefficient of Variation (% Std. Deviation)
H_2S	5
H_2S - SO_2	5
SO_2	10
NO_x	10
CO	10
H_2O	10
CO_2	5
O_2	5
HCN	10

All tube readings were repeated with a tube of a different span capacity.

Readings were corrected for interference by subtractive method. (No correction was made for mercaptans in H_2S evaluations.) (See Ref. 5)

Additionally, the inorganic fraction of particulate samples collected by wet impingement was analyzed for trace metallic elements by a consulting laboratory using X-ray fluorescence instrumentation for trace metal emissions.

SECTION 4.0

TEST RESULTS AND EMISSION FACTOR CALCULATIONS

The treatment of the results of tests and calculations of emission factors is divided into two steps. The first step is to develop steam generator emission factors on the basis of the fuel oil burned by analyzing the steam generator emission test results provided by producers and local authorities plus KVB test data generated on this and another program. We will compare these emission factors with those in the EPA's document AP-42 (Ref. 2) and show that the emission data measured on this program are reasonably consistent with previous test data and AP-42.

The second step is to compute emission factors related to the oil production rate. Here we sum the emission we measured in the field for both steam generators and well vents and prorate them to the oil production data that were provided by the oil companies. This gives us pounds of pollutants per barrel of oil produced for both the steamflooding and fireflooding operations.

Finally, we will present other test data which will demonstrate some techniques for reducing NO_x emissions and evaluate scrubber performance at San Ardo.

In this report we have included all of the data from tests under consideration including raw work sheets which may be found in the Appendix of this report.

4.1 EMISSION FACTORS

An emission factor may be defined as a number which relates the mass of a pollutant produced to some measure of process throughout; in this case, either:

1. The amount of fuel consumed, i.e., lbs. of pollutant/1000 gallons fuel;
2. The amount of heat produced, i.e., lbs. of pollutant/10^6 BTU, or
3. The amount of crude oil produced, i.e., lbs. of pollutant/bbl. crude oil produced.

Steam generation equipment pollution testing can be accomplished with good accuracy and precision which will yield reliable pollution factors for 1 and 2 above in any given test situation. Emissions produced by the air compressors used by fireflooding operators may also be very accurately assessed. However, while California crudes are similar in composition, they are not the same. Determining statewide emission factors based on amount of crude produced from a few tests involving a single oil reservoir can produce errors. Errors may be minimized only by performing more tests on more reservoirs using different types of steam generating equipment in actual use.

The amount of crude oil produced in any TEOR operation will vary with the size of the field, the composition and physical characteristics of the crude to be stimulated. In the case of fireflooding it is very difficult to estimate accurately the extent of the reservoir so flooded and to determine specifically which wells are benefitted by the thermal stimulation process.

In the case of Mobil Lost Hills fireflooding, the program budget could only afford sampling of five of the forty wells. We selected the five to span the field locationwise and found that they also spanned the output rates and output temperatures. We feel that the range of these emission rates sampled tend to lend some credibility as to representativeness of our emission factors.

The crude oil production rates used in deriving emission factors were supplied by the producers. They represent their best estimate of the results of thermal stimulation. From their extensive experience these figures gain reliability and the emission factors in this report relating to crude oil produced represent, in our opinion, the most reliable estimate to date.

4.1.1 Steam Generator Emission Factors - Lb/1000 Gal

A summary of the available emission factor data for $50x10^6$ Btu/hr steam generators is presented in Table 4-1. For comparative purposes, that portion of this report dealing with oil field steam generators is limited to the $50x10^6$ Btu/hr size. It is understood that this is the most popular size package boiler for future oil field operations. Items 16a, 16b, and 17 are tests performed by KVB on this program. All other data in the table were supplied by oil producers, local pollution authorities or the California Air Resources Board, as noted.

To properly evaluate the data in Table 4-1 it is important to realize that each line of data reported is characteristic of a particular steam generator operating in an as-found condition at varying loads and levels of excess O_2. However, normally these units are operated at close to full load (80 to 100% of rated capacity, 50 million BTU/hr). The excess O_2 levels vary between 3 and 8% which primarily accounts for the variation in NO_x emissions. The emission factors reported are the normal or as-found values. Therefore the average values shown are the average as-found emission factors.

The steam generators in Monterey County are equipped with sulfur scrubbers. Table 4-1 reflects data measured both at the inlet and outlet of the scrubber as indicated in the "Comments" column. Generally, the non-sulfur gaseous emissions are unchanged by the scrubber, i.e., NO_x, CO, and H/C. The particulate emissions on the KVB/ARB test (Nos. 16a and b, Table 4-1) were reduced from half (for the solid catch) to two-thirds (for the total catch) by the water scrubber used by Mobil.

A summary of emission factors data is presented in Table 4-2. The data from the two KVB/ARB tests are compared with the average data from Table 4-1

TABLE 4-1. 50mm Btu/Hr TEOR STEAM GENERATOR TEST DATA

ITEM NO.	OPERATOR	COUNTY	TESTED BY	YEAR	REF. NO.	EMISSION FACTORS, LB/10^3 GAL FUEL BURNED: PARTICULATE SOLID/TOTAL	SO_x (1)	CO	HC	NOx	SULFUR %	COMMENTS
1	Belridge	K	Kern APCD	1974	6	- /16.6	-	-	-	-	1.15	
2	Belridge	K	Kern APCD	1974	7	- / -	-	-	-	80.1	1.15	
3	Chevron	K	Chemecology	1974	8	11.0 /14.4	153.1S	0.8	17.9	33.8	1.1	
4	Tenneco	K	Kern APCD	1975	9	- /17.3	-	-	-	-	1.4	
5a	CWOD	K	RETA	1977	10	14.0 / -	137.5S	5.0	0.8	36.3	1.39	Lease Crude
5b	CWOD	K	RETA	1977	10	9.9 / -	138.5S	4.1	1.6	38.0	0.87	Lease Crude + Low Sul. Resid.
5c	CWOD	K	RETA	1977	11	7.8 / -	164.4S	3.1	1.6	30.7	0.41	Low Sulfur Residual
6a	Mobil	M	CARB	1977		- / -	167.0S	-	-	-	3.56	Scrubber (Inlet)
6b			CARB	1977	11		23.4S	6.9		68.1	3.56	Scrubber (Outlet)
7a	Mobil	M	CARB	1977			179.3S	-			1.83	Scrubber (Inlet)
7b			CARB	1977	11		25.1S	6.9		57.4	1.83	Scrubber (Outlet)
8a	Texaco	M	CARB	1977			158.4S	-		-	1.70	Scrubber (Inlet)
8b			CARB	1977	11		49.1S	6.9		65.7	1.70	Scrubber (Outlet)
9a	Texaco	M	CARB	1977			129.4S	-		-	1.84	Scrubber (Inlet)
9b			CARB	1977	11		45.3S	-		42.6	1.84	Scrubber (Outlet)
10a	Texaco	M	CARB	1977			164.1S	-		-	1.88	Scrubber (Inlet)
10b			CARB	1977	11		36.1S	-		57.7	1.88	Scrubber (Outlet)
11a	Texaco	M	CARB	1977			145.5S	-		-	1.87	Scrubber (Inlet)
11b			CARB	1977	12		32.0S	-		51.6	1.87	Scrubber (Outlet)
12	Various	K	Various	1977	13	13.6/ -	159.5S	< ..2	<0.2	78.6	1.1	
13	Mobil 24-3	M	KVB	1978	13	24.8/27.8	-	-	-	-	2.18	Scrubber (Outlet) Weak NaOH
14	Mobil 24-4	M	KVB	1978	13	21.9/25.6	16.4S	-	-	-	2.25	Scrubber (Outlet) Weak NaOH
15	Mobil 24-5	M	KVB	1978		22.0/24.0	12.0S	-	-	-	2.20	Scrubber (Outlet) Weak NaOH
16a	Mobil (3)	M	KVB	1978		20.3/40.3	172.8S	9.6	1.0 (2)	35.5	2.24	Scrubber (Inlet)
16b			KVB	1978		10.9/14.0	30.2S	10.4	1.0 (2)	38.4	2.24	Scrubber (Outlet), Produced Water
17	Tenneco (3)	K	KVB	1978		8.6/21.1	149.0S	4.5	0.9	50	1.0	Average of 2 Tests
AVERAGE						15 /23	155 (4)	5.8	1.02	51	1.77	

(1) S = Sulfur in Weight %
(2) Below Background level
(3) KVB/CARB Programs
(4) Average Uncontrolled (i.e. Excludes Scrubber Outlet Data)

K = Kern County
M = Monterey County
TEOR = Thermal Enhanced Oil Recovery

TABLE 4-2. EMISSION FACTORS FOR TEOR STEAM GENERATORS ON THE KVB/CARB PROGRAM

(Lb Pollutant/10^3 Gallons Crude Burned)

	Mobil, San Ardo Scrubber Inlet	Tenneco, Kendon No Scrubber	Average From Table 4-1	AP-42 Residual Oil (Ref.2)
Particulates (Front End Only)*	20.3	8.6	15 (8S+3)**	10 S+3
SO_2	173 S	149 S	155 S	157 S
SO_3	6 S	7 S	---	2 S
CO	9.6	4.5	5.8	5
Hydrocarbons	1	1	1	1
NO_x	36	50	51	60
Fuel Sulfur	2.3	1.0	1.77	N/A

TEOR = Thermal Enhanced Oil Recovery
S = Fuel Sulfur, Wt %
N/A - Not Applicable

*Filter Only
**Refer to Figure 4-1

and the emission factors from the EPA's Publication AP-42 for industrial boilers burning residual oil. Generally, the agreement with AP-42 is good. The variation in SO_2 factors measured on the KVB/ARB tests can be explained by difficulties in fuel oil sampling and differences in fuel density. It was difficult to maintain constant fuel flow to the generators because of trapped gases in the crude oil. The feed pumps were often heard to cavitate and the excess O_2 readings showed frequent oscillations. This effect was more pronounced at Mobil than at Tenneco.

Mobil San Ardo crude sampling was complicated by H_2S and other gases in the oil. Crude oil samples exhibited frothing, indicating that significant sulfur-containing gas may have escaped resulting in a low value for sulfur content. Also, since the emission factors are expressed in volumetric units, i.e., per 1000 gals, and the fuel sulfur is in weight percent, the greater the density of the fuel, the higher will be numerical coefficient of the emission factor. The Mobil San Ardo gravity was degree API 11 while the Tenneco was 13.7 (respectively 8.1 and 8.3 lb/gal). A typical #6 fuel oil would run degree API 15 or 8 lb/gal.

The particulate emission factors for those crude-fired units shown in Table 4-2 also show a small difference from the AP-42 relationship. Note that the particulate emission factors in Table 4-2 are for the solid (filter or "front end") catch only, meaning they do not include the impinger catch. This was presented in this manner because the AP-42 data are based on EPA's Method 5 procedures which use only the filter catch and ignore the impinger catch.

Figure 4-1 shows a plot of emission factor vs. sulfur content with the AP-42 curve and the data from Table 4-1 plotted. The plotted crude oil data points generally fall below the AP-42 curve. Interestingly, the one point for a steam generator fueled with #6 residual oil (labeled "Low Sulfur Residual Oil") falls very close to the AP-42 curve while the point for that same unit burning crude (labeled "Lease Crude") falls below the AP-42 curve. These data suggest a modified relationship for crude oil fired boilers of 8S+3 instead of the 10S+3 given by AP-42 for #6 residual oil. The crude oil curve is also plotted on Figure 4-1.

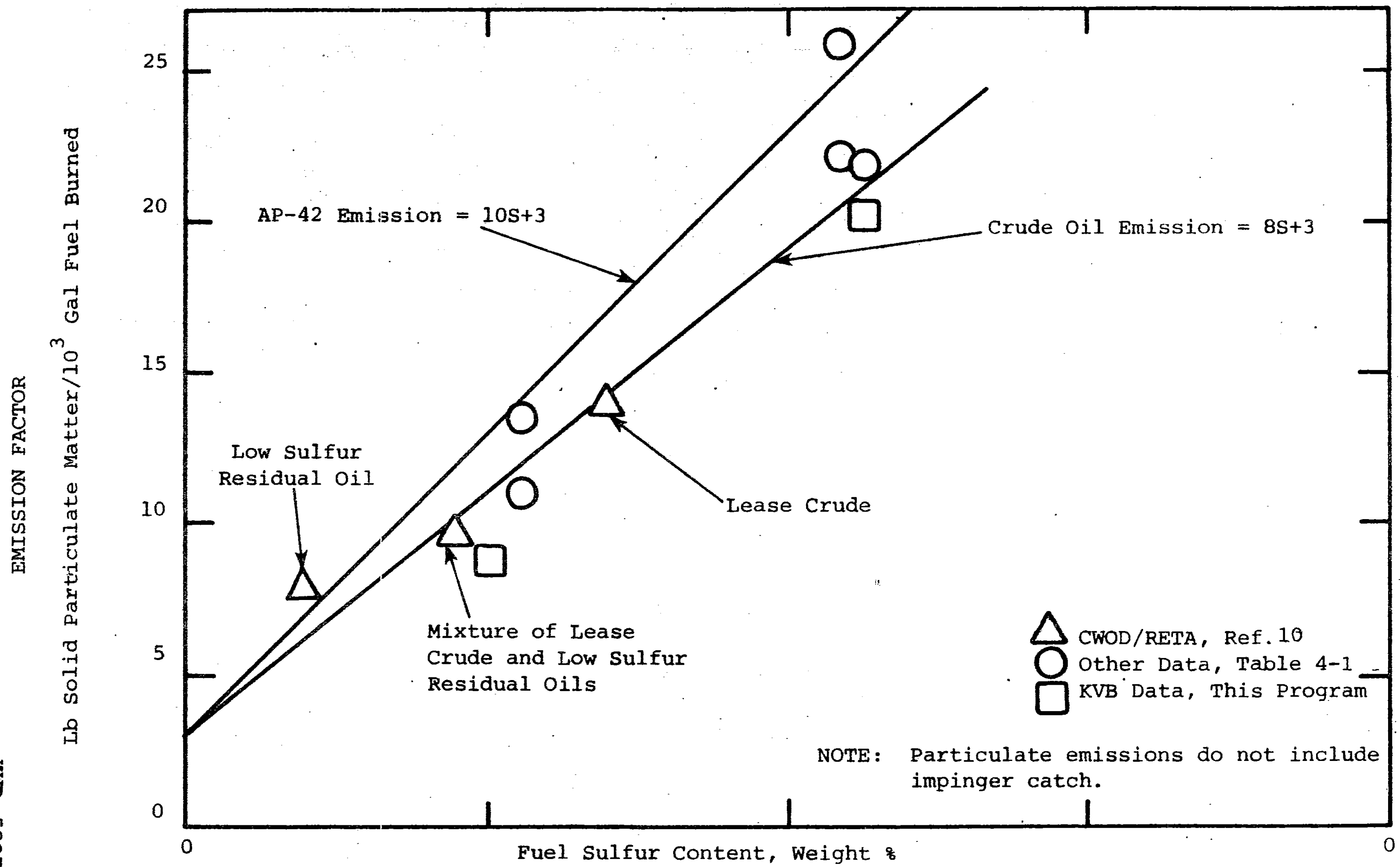

Figure 4-1. Effect of fuel sulfur on particulate emissions for crude-oil-fired TEOR steam generators.

The hydrocarbon emissions listed in Table 4-2 are those measured by a flame ionization detector (FID). As discussed below, the organic fraction extracted from the impinger on the particulate train is also included as part of the total hydrocarbons. However, the steam generator flue gas had no measurable organic fraction in the particulates catch. The FID tests on the steam generators indicated very low concentrations (approximately 20 ppm). In fact, at San Ardo the hydrocarbon concentration measured from the steam generator stack was lower than that in the ambient air. Since the emitted concentration of hydrocarbons would be unaffected by the low background concentations, the directly measured concentration was reported in Table 4-2 and used for emission factor calculation.

4.1.2 Emission Factors Based on Crude Oil Produced

In this section the emission from TEOR operations are related to the oil production rate. In the previous section the steam generator emissions were presented as a function of fuel consumed. For individual steam generators or thermal recovery projects whenever possible, emissions should be calculated on the basis of fuel consumption. However, when estimated oil production rate is the only available parameter then a rough estimate of the emissions can be made from the emission factors in this section. The problem is that the fuel required to produce a net barrel of production can vary widely as a function of reservoir characteristics and how long a given thermal recovery operation has been conducted in a specific reservoir.

The emissions included in the emission factors presented in this section include those of the well vents, air compressor well as those of the steam generators.

Table 4-3 presents the emission factors for the steam generators, well vents and fireflood air compressor all on the basis of pounds of pollutant per barrel of crude produced. The steam generator emissions were computed using the ratio of crude oil produced to crude oil burned for TEOR as provided by the respective oil companies. These ratios are presented at the bottom of Table 4-3 (Ref. 14, 15, & 16).

TABLE 4-3. TEOR EMISSION FACTORS IN POUND POLLUTANT PER BARREL OF CRUDE PRODUCED

Pollutant	Mobil* San Ardo S.G. Scrub. In	Mobil* San Ardo S.G. Scrub. Out	Tenneco* Kendon S.G. (No Scrub.)	CWOD Midway Sunset Well Vents	Mobil Lost Hills Compressor	Mobil Lost Hills Well Vents
Total Particulates (Condensible HC)	0.47 (0)	0.28 (0)	0.185 (0)	0.095 (0.090)	No Data Available	0.15 (0.15)
HC (Non-Condensible)	0.01	0.01	0.01	0.0004	0.02	0.23
TOTAL HC (Cond.+ Non-Cond.)	0.01	0.01	0.01	0.09	0.02	0.38
SO_2	2.0 S	0.44 S	1.33 S	0	0	0.03
SO_3	0.07 S	0.04 S	0.07 S	---	---	---
CO	0.112	0.123	0.04	0	0.007	0.002
NO_x	0.42	0.44	0.45	0	0.05	0
H_2S	0	0	0	0.0003	0	0.03
Fuel Sulfur Wt %	2.25	2.25	1.0	1.0	--	--
Ratio, Barrels Oil Produced/Barrel Oil Burned for TEOR (Gross)	3.6 (Ref.14)	3.6 (Ref. 14)	4.7 (Ref. 15)	5.2 (Ref. 16)	N/A	N/A

S = Sulfur in Weight %
TEOR = Thermal Enhanced Oil Recovery

*Emission factors based on fuel consumption are presented in Table 4-2. When fuel consumption data are available, the emissions from individual steam generators and thermal recovery projects should be calculated on the basis of fuel consumption.

Note that unlike Table 4-2, the particulates emission factors in Table 4-3 are based on the total catch which means they include the material collected in the impinger train. All of the data in Table 4-2 were measured by KVB during this program except those for the fireflood compressor at Lost Hills.

The fireflood compressor emissions (Table 4-3) are based on AP-42 emission factors and the fuel comsumption rate provided by the oil company, details as provided in Table 4-4. The compressors run on field gas; 75% (vol) methane, 3% ethane, 20% CO_2, and 2% other hydrocarbons. Sulfur content is approximately 0.5 grains/10^3 ft^3. The annual gas consumption for the two 600 HP and one 350 HP units is 80×10^6 SCF/yr. The average daily crude oil production at Mobil Lost Hills is 12,000 barrels. AP-42 provides no data on particulate emissions for gas-fired internal combustion engines. For gas firing, the particulate emission should be negligible if the engines are properly tuned.

The hydrocarbons emitted from the well vents shown in Table 4-3 were measured by two methods, the results of which must be added together to obtain the total hydrocarbon emissions. The condensible hydrocarbons were collected in a Method 5 impinger without the use of a filter which usually proceeds the impinger. The impinger was filled with water at a temperature of 50° to 60°F. The condensed hydrocarbons were extracted from the impinger using methyl chloroform. The gaseous hydrocarbons listed in Table 4-3 were sampled using glass collection bottles and analyzed by gas chromatograph. The contents were over 90% methane and therefore non-condensible. Thus the total hydrocarbon emissions are obtained by adding the two components as indicated on the table.

Table 4-5 summarizes the emission for steam and fireflooding. The reader is again cautioned that these results are based on very few tests at one location and should be treated as a qualitative indication of emissions. More test data should be obtained before any final conclusions are drawn with regard to emission factors.

Preliminary as they are, however, these data show that, as a concept, fireflooding, using large gas-fired compressor engines, produces considerably

TABLE 4-4. CHARACTERISTICS OF FIREFLOODING OPERATIONS AT MOBIL LOST HILLS

Compressors
Fuel type - field gas (800-900 Btu/SCF)

Fuel composition (approximate)

CH_4	-	75.5% by volume
C_2H_6	-	3 % by volume
CO_2	-	19-20% by volume
Trace HC's	-	2-3 % by volume
sulfur content	-	500 grains/10^6 SCF

Compressor size -

1X550 HP

2X350 HP

Total field gas consumption -

estimated @ $80X10^6$ SCF/yr.

Emission factors based on AP-42 (Ref. 2)

Pollutant	NO_x	CO	HC	SO_2	TSP
lbs/10^6SCF	2700	350	1100	.15	negligible
Annual Emissions in pounds	$216X10^3$	$28X10^3$	$88X10^3$	12	
Daily emissions (lbs.) (360 day year)	600	78	244	negligible	

Other Data

Oil Produced: 12,000 bbl/day

Total No. Producing Wells: 41

Ratio, bbl Oil Produced/1000 ft^3 Injected = 6.6

TABLE 4-5. INTEGRATED EMISSION FACTORS FOR STEAMFLOODING AND FIREFLOODING OPERATIONS
LB POLLUTANT/BBL CRUDE PRODUCED

	STEAMFLOODING			FIREFLOODING		
	Steam Generator (Uncontrolled) Avg. of Mobil & Tenneco*	Well Vents (CWOD)**	Total**	Compressor (Mobil-Lost Hills Natural Gas Fuel)**	Well Vents (Mobil - Lost Hills)**	Total**
TSP (Condensible HC)	0.33(8S+3) (0)	0.095 (0.09)	0.43 (0.09)	Negligible	0.15 (0.15)	0.15 (0.15)
HC (Gaseous)	0.01	(0.0004)	0.0054	0.02	0.23	0.25
TOTAL HC	0.005	0.09	0.095	0.02	0.38	0.40
SOx as SO_2	1.7 S	(0)	1.7 S	Negligible	0.03	0.03
CO	0.076	(0)	0.076	0.007	0.002	0.009
NOx as NO_2	0.43	(0)	0.43	0.05	(0)	0.05
H_2S	(0)	0.0003	0.0003	(0)	0.03	0.03
HCN	(0)	(0)	(0)	(0)	0.0002	0.0002
Fuel Sulfur Weight %	1.6	1.0		N/A	N/A	

S = Fuel Sulfur in %
N/A = Not Applicable
TEOR = Thermal Enhanced Oil Recovery

*Emission factors based on fuel consumption are presented in Table 4-2. When fuel consumption data are available, the emissions from individual steam generators and thermal recovery projects should be calculated on the basis of fuel consumption.

**These data are based on very few tests and should be treated as a qualitative indication of emissions.

less total emissions than steamflooding. Only the hydrocarbon and H_2S emissions of the fireflooding exceed those of steamflooding. Fireflooding is known to produce odorous emissions.

4.2 TRACE METAL CONTENT

At each location tested for particulates on the KVB/ARB program, trace element contents were determined by x-ray fluorescence (XRF) on those catches 100 mg or greater. XRF is an inexpensive, multi-element, analytical technique with modest accuracy and definite limitations. Therefore, the data should be treated as semi-quantitative.

The XRF results are summarized in Table 4-6. Detailed XRF analyses reports are in the Appendix. Of greatest interest here are the trace metals. Many of the other important elements, which are included in the composition of these particulates, were not detected by the XRF analytical technique used. These are listed at the bottom of Table 4-6. The most significant of these are carbon, oxygen, silicon, nitrogen, sulfur and aluminum. In most instances these missing compounds represent over 95% of the matter collected. The elements with prominence in Table 4-6 are iron, chlorine, nickel, vanadium and calcium. Iron is most prevalent probably because of deterioration of the pipes and ducts conducting the emissions. Nickel and vanadium are trace elements in the crude. Chlorine and calcium were found primarily in the steam vent emissions no doubt dissolved in the connate water which is produced with the the crude oil.

4.3 OTHER TEST DATA

4.3.1 Nitrogen Oxide Data

It is a well established fact that NO_x emissions from boilers are affected by the amount of excess O_2 (i.e., the amount of O_2 in excess of the theoretical stoichiometric ratio) used in the combustion. The simplest form of combustion optimization on a boiler is to adjust the air/fuel ratio to as low a value as possible. The "lowest possible" value occurs either (1) when the CO emissions, which are normally less than 50 ppm, begin to increase rapidly as the O_2 level is reduced, or (2) when the unit begins to make smoke.

TABLE 4-6. X-RAY FLUORESCENCE (XRF) ANALYSIS OF PARTICULATE EMISSIONS FROM TEOR SOURCES, WEIGHT %

Element	STEAM GENERATORS: Mobil San Ardo			STEAMFLOOD: CWOD Midway Sunset		FIREFLOOD VENT: Mobil Lost Hills		
	Mobil San Ardo		Tenneco	CWOD Midway Sunset		Test I		Test II
	Filter At Inlet	Filter At Outlet	Filter	Impinger @ Condenser	Impinger @ Well Vent	Filter	Impinger	Impinger
Arsenic	0.01	0.008	0.14					0.01
Barium	0.01			0.2	3.5		0.03	0.21
Bromine				(0.002)			0.01	0.02
Cadmium				0.005	(0.002)		0.004	0.04
Calcium	1.1	(4.1)	(27)	0.62	10.	(5.9)	0.56	0.92
Chlorine				5.	2.7		15.	35.
Cobalt	0.02							(0.03)
Copper				0.01	0.02		0.006	0.09
Gallium	0.04	(0.04)	0.1					
Iron	1.0	0.25	6.6	20.	0.93	72	6.8	1.1
Lead	(0.003)	(0.006)	(0.005)	0.005	0.003	(0.16)	0.007	0.04
Manganese	(0.02)		(0.10)	0.22			0.06	(0.02)
Mercury	(0.002)	(0.003)		(0.01)	0.09		(0.003)	(0.01)
Molybdenum	0.07	0.04		0.003	(0.004)			
Nickel	1.6	1.3	9.0	0.01	(0.005)	(0.11)	0.03	0.04
Niobium				(0.001)				
Potassium	0.2						0.16	0.8
Rubidium				(0.004)				
Selenium	(0.001)	(0.002)	(0.03)	(0.002)	0.002		0.001	
Silver	0.006			0.003				
Strontium	0.02	0.04	3.0	0.003	0.09		0.01	
Titanium	0.1	(0.1)	(0.6)	(0.08)				
Vanadium	2.7	1.2	2.1					
Yttrium	(0.005)							
Zinc	0.04	0.05	0.15	0.04	0.05		0.07	0.32
Particulate Emission Factors	20.3 lb/1000 gal_S Burned 0.24 lb/bbls Produced	10.9 lb/1000 gal_S Burned 0.13 lb/bbl^S Produced	8.6 lb/1000 gal_S Burned 0.077 lb/bbl^S Produced	0.095 lb/bbl^T Produced	0.095 lb/bbl^T Produced	0.0025 lb/bbl_S Produced	0.15 lb/bbl_C Produced	0.15 lb/bbl_C Produced

Notes: 1. ( )= Best estimate
2. All others - Not Detected
3. Mobile Fireflood Test - insufficient filter catch, 100 mg required for analysis
4. S = Solid, C = Condensable, T = Total, TEOR = Thermal Enhanced Oil Recovery
5. Important Elements not detected by XRF: Lithium, Beryllium, Boron, Carbon, Fluorine, Sodium, Nitrogen, Magnesium, Aluminum, Silicon, Phosphorus, Sulfur, Oxygen

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Figures 4-2 and 4-3 are plots of NO_x concentration as determined by the TECO instrument versus the percent of excess O_2 as determined by the Teledyne analyzer for the two steam generators tested on the program. The NO_x has been adjusted to reflect a concentration equivalent to 3% O_2 so that the change in NO_x concentration reflects the absolute change and not a dilution effect. Note that at Mobil San Ardo (Figure 4-2) as the excess O_2 drops below approximately 1.5% the CO concentration begins to rise dramatically. At Tenneco (Figure 4-3) as the excess air dropped below 2% the unit began to smoke noticeably. At San Ardo any tendency to smoke may have been obscured by the scrubber. From these results it is apparent that the units should be operated at an excess O_2 level of 2%. Actually, with some burner modifications and a tuneup, it might be possible to operate these units at close to 1% excess O_2 without excessive CO or smoking.

The problem with operating these oil field steam generators at low O_2 levels is that they are unattended and they usually burn lease crude which vary widely in composition and purity. In operating close to the threshold smoke level for O_2 adjustment there is a real possibility that a perturbation in the oil properties or burner hardware will occur. This can cause the unit to smoke until a suitable adjustment can be made to the burners. To avoid this smoking condition, which can be easily detected by the Air Pollution Control District personnel, the O_2 controls are set up to a level at which the unit can handle these fuel fluctuations without smoking.

4.3.2 Mobil San Ardo Scrubber Data

The sulfur scrubber on the steam generator tested at Mobil San Ardo as discussed earlier has a very simple concept. The flue gases from the generator are ducted through a spray tower fed by the naturally-occurring connate water that is produced with the crude oil. The connate water contains carbonates, chlorides, and other minerals that react with the SO_2 in the flue gases. Table 4-7 is a summary of the SO_2 data taken during the San Ardo test upstream and downstream of the scrubber. The stoichiometric concentration is the theoretical concentration if all of the fuel sulfur were converted to SO_2.

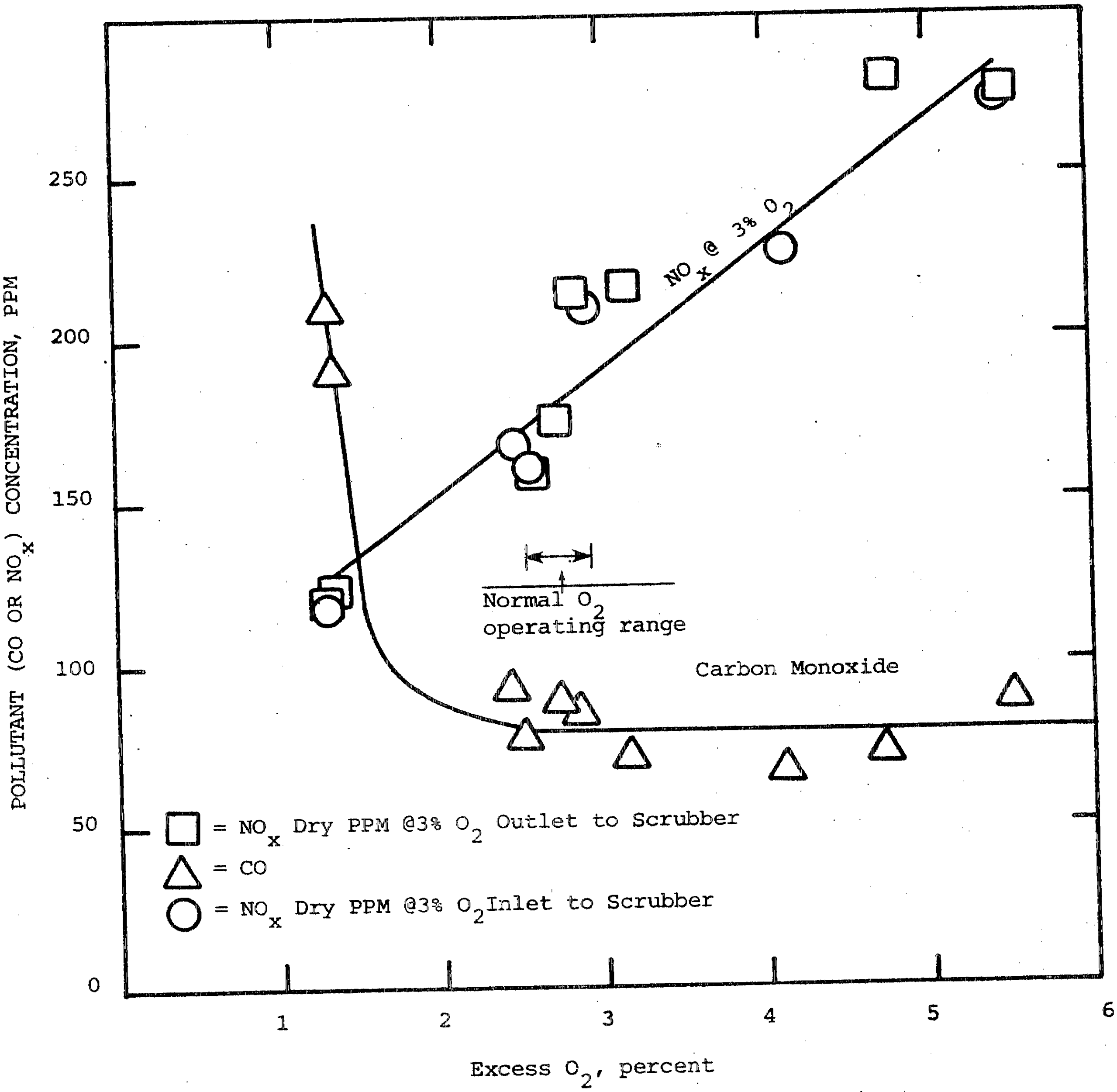

Figure 4-2. Effect of excess O_2 on NO_x emissions for Mobil-San Ardo steam generator No. 22-5.

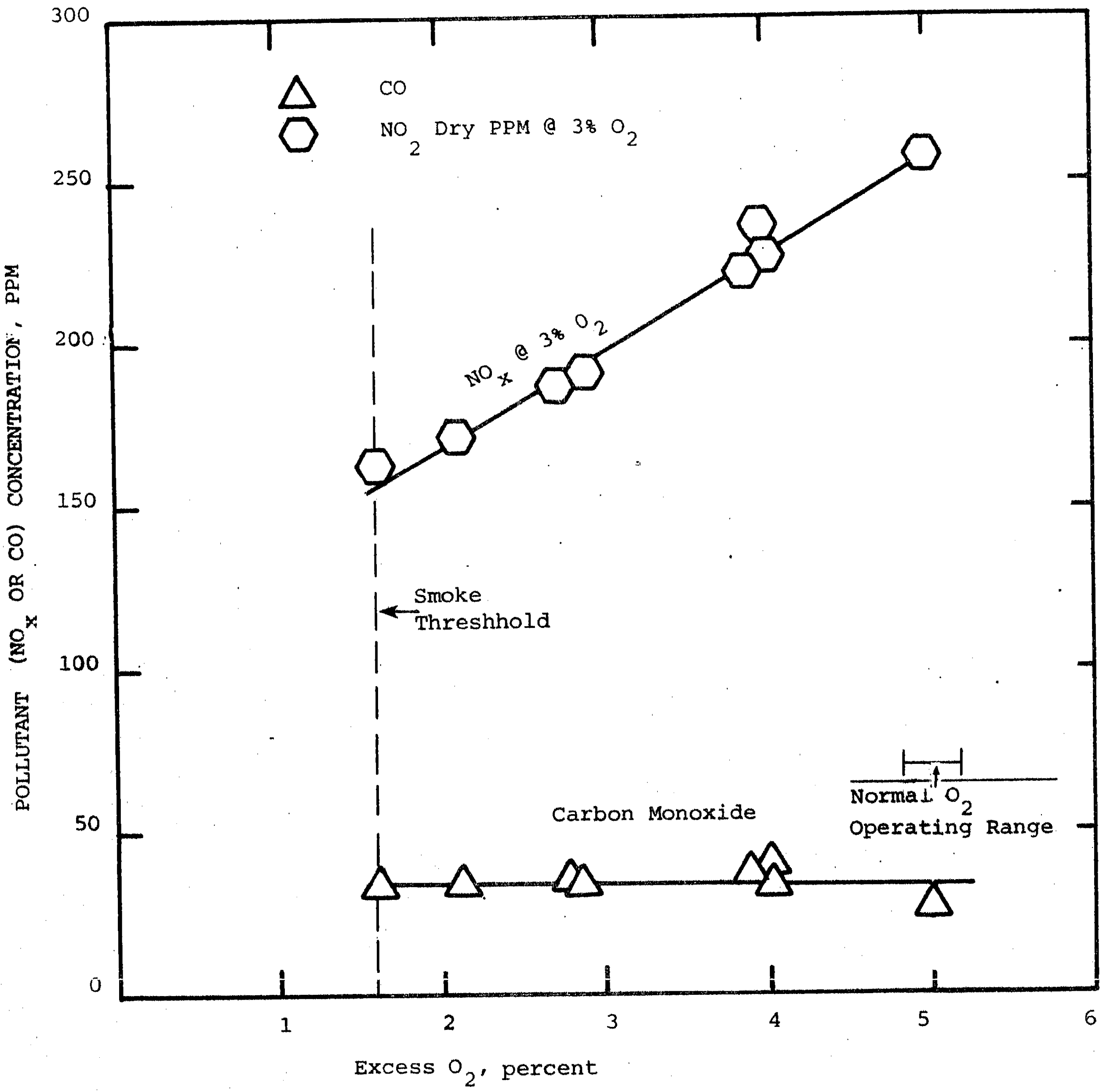

Figure 4-3. Effect of excess O_2 on NO_x emissions for Tenneco Kendon. steam generator No. 43.

TABLE 4-7. MOBIL SAN ARDO SCRUBBER DATA

Excess O_2 Scrubber Inlet %	Stoichiometric SO_2 Conc. Based on Listed O_2, PPM	SO_2 Measurements w/ DuPont 400 Analyzer, PPM			SO_2 Removal Efficiency, %
		Scrubber Inlet	Scrubber Outlet		
1.7	1410	1581	414		74
2.6	1370	1456	252		83
2.6	1370	1392	283		80
3.6	1320	1317	311		76
5.4	1220	1130	168		85
				Average	80

Fuel Sulfur: 2.24% Scrubbing Medium: Connate Water

This number should be a few percent higher than the concentration measured upstream of the scrubber. The agreement between these numbers varies from plus 11% to minus 7%. The greatest disagreements are in the top and bottom rows. Since these two disagreements are in different directions, they tend to cancel each other in the determination of scrubber efficiency which appears to leave a solid average of 80%.

SECTION 5.0

ESTIMATED EMISSIONS FOR TEOR OPERATIONS IN CALIFORNIA

According to the Conservation Committee of California Oil Producers (CCOP) TEOR operations were started in California in 1963 and by 1977 the TEOR gross production had increased to 183,000 bbl/day (Ref. 17). According to Science Applications Incorporated (SAI) of La Jolla, Reference 30, the 1977-1978 California thermal oil production average 230,000 bbl/day. With increasing crude oil prices, price decontrols on heavy oil, etc., a large increase is planned in the number of steam generators. SAI maintains an ongoing inventory of steam generators for Kern County, CA, the area of greatest TEOR activities in the State. They provided us with their inventory as of August, 1979 (Ref. 18). At the same time we obtained an inventory of steam generators from the Monterey Bay Unified APCD (Ref. 19). A summary of this information is presented in Table 5-1. The steam generators in the SAI inventory were categorized as existing or new. The new units, which approximately equal the existing units, are the subject of some regulatory action by the ARB and local air pollution control agencies. We understand, however, that permits for these units will be issued and they are in various states of installation from on-order to operational. When all of these units are installed (probably in 1981 or 1982), the total steam generator rated capacity in the State will be approximately 44×10^9 Btu/hr. Table 5-1 also shows the corresponding fuel consumption for these steam generators assuming that they operate at 80% of rated capacity which is the usual case and assuming 20% down time for routine maintenance etc. (80% on stream) (Ref. 20).

The total fuel consumption for the units listed in Table 5-1 is 148,000 bbl/day. It is generally believed (see for example Ref. 20) that the ratio of crude oil produced to crude oil burned in the steam generators is from 3 to 4 gross or 2 to 3 net where the high numbers include the crude

TABLE 5-1. SUMMARY OF OIL FIELD STEAM GENERATOR CAPACITY AND FUEL CONSUMPTION FOR KERN AND MONTEREY COUNTIES, CALIFORNIA AS OF AUGUST, 1979

Location	Rated Capacity 10^6 Btu/hr			Fuel Consumption @ 80% of Rated Capacity and 80% on Stream Time bbl/day		
	Existing	New	Total	Existing	New	Total
Central Kern County *	9,000	13,000	22,000	30,000	44,000	74,000
Westside Kern County *	11,000	8,000	19,000	37.000	27,000	64,000
Monterey County †	3,000	0	3,000	10,000	0	10,000
		Total	44,000		Total	148,000

Sources: * Science Applications Inc. (Ref. 18)
† Monterey Bay Unified APCD (Ref. 19)

burned as part of the crude produced and the lower numbers do not include the crude burned as a part of the crude produced. Although our observations (see Table 4-3) tend to be on the high end of this range we will use a ratio of 3 gross or 2 net for further analysis since this is the value that the industry feels is more representative.

Based on the 148,000 bbl/day fuel consumption from Table 5-1 and a ratio of 3, the gross production of crude oil calculates to be 440,000 bbl/day. SAI (Ref. 31) estimates 464,000 bbl/day for TEOR in Regions 3 and 4 (California Division of Oil and Gas {DOG} designations) which are primarily Kern and Monterey counties with regard to TEOR.

Other numbers with which to compare are an estimate made in 1978 by the U.S. Congressional Office of Technology Assessment (OTA) (Ref. 21) and the U.S. Department of Energy (DOE) 1985 goal for statewide production. The OTA estimated the potential oil recovery from TEOR operations (primarily in California) to the year 2000 as follows:

	10^9 Barrels
Steamflood (net Recoverable)	3.9
Steamflood (Fuel Consumption)	1.3
Steamflood (Gross Recoverable)	5.2
Fireflood	1.1
Total Recoverable	6.3

Dividing the 5.2 x 10^9 barrel gross recoverable estimate by 20 years and 365 days per year the average daily production calculates to be 710,000 bbl/day. DOE's 1985 goal for California TEOR is in excess of 900,000 bbl/day (Ref. 30).

Using the above information and estimate, a forecast of the TEOR production rates was prepared as shown in Figure 5-1. The constructed curve begins with the SAI curve from Reference 32. Indicated on the figure is the CCOP point for 1977 (Ref. 17) which disagrees with the SAI curve. The SAI report data were favored because they were obtained from the California DOG. The middle segment of the curve was constructed based on the 440,000 bbl/day estimate calculation from the SAI steamer inventory and the SAI estimate of 464,000 bbl/day for TEOR in 1985. The 440,000 bbl/day was estimated to be

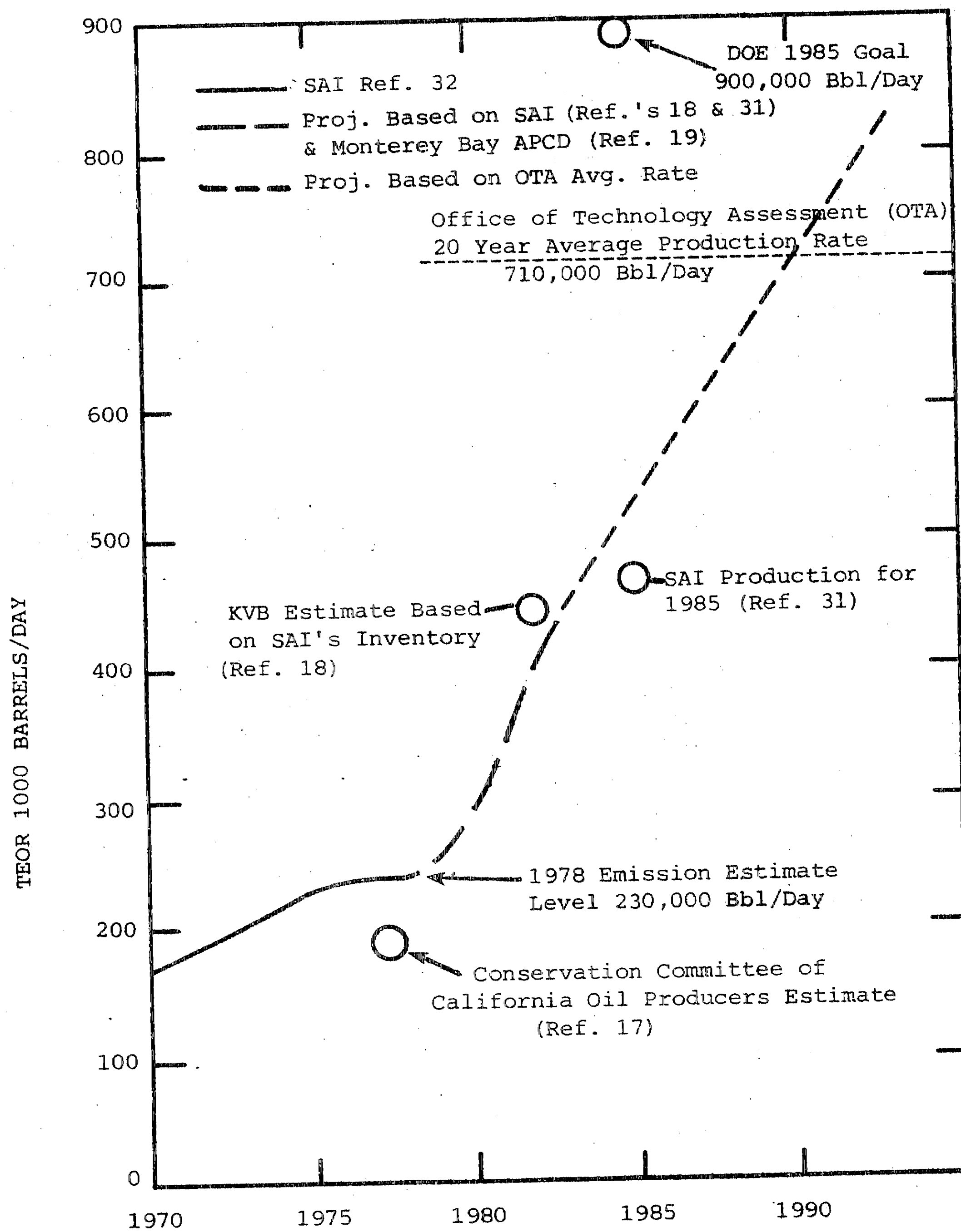

Figure 5-1. Kern & Monterey County TEOR estimate and forecast.

achieved by 1982. The final segment of the curve was constructed to intersect with the 710,000 bbl/day line in 1990 in order to achieve the OTA predicted average at the midpoint between 1980 and 2000.

To estimate emissions we picked a plateau on the curve shown in Figure 5-1 at a production rate of 230,000 bbl/day and used the emission factors developed on the program. For the steam generators we used the average factors from Table 4-1 as follows:

Pollutant	lb/1000 gal
TSP	
Solid	8S+3
Total**	23
SO_x as (SO_2)	155 S*
CO	5.8
HC (non-condensible)**	1
NOx	51

*S - Percentage sulfur in fuel oil.
**TEOR steam generators in normal operating condition emit no condensible hydrocarbons.

For the total TEOR emission we used the factors in Table 4-5 as follows:

Pollutant	lb/bbl produced	
	Steamflood	Fireflood
TSP (total)	0.43	0.15
(condensible HC)	(0.09)	(0.15)
HC (non-condensible)	0.0054	0.25
Total HC (cond & non-cond)	0.095	0.40
SOx	1.7 S*	0.03
CO	0.076	0.009
NOx	0.43	0.05
H_2S	0.0003	0.03

*S = % Sulfur in crude oil burned

Emissions calculated assuming no controls are tabulated in Table 5-2 along with estimates by other activities. The KVB estimates are in the first, fifth and sixth columns and are based on the installed capacity as shown in Table 5-1 assuming all of it is operational. Column 1 lists the emissions just from the steam generators themselves ignoring well vent emissions. These were calculated from the average emissions factors from Table 4-1, as listed above, and a fuel consumption rate of 77,000 bbl/day which corresponds to a TEOR production rate of 230,000 bbl/day.

Column 2 lists emissions as estimated by the ARB in a staff report dated April 26, 1978. The ARB's 250 ton/day for SOx was based on controls established by the Kern County APCD which would require offsets or scrubbers to limit SO_2 emissions.

Column 3 lists emissions in an impact assessment by SAI for the proposed new steam generators in the Westside Kern County area (Ref. 20). To scale this up to the full Kern County and Monterey County areas these emissions were increased by a factor of 44/19, which is the ratio of total steam generator capacity to Westside Kern County capacity as indicated in Table 5-1. These scaled-up numbers are in Column 4.

Columns 5 and 6 in Table 5-2 are the total emissions calculated for steamflood and fireflood TEOR operations and respectively account for steam generator, air compressor and well vent emissions. The steamflood emissions were based on the reported 230,000 bbl/day gross crude oil production for 1977 and 1978, and the emission factors from Table 5-6. The fireflood emissions were calculated based on an assumed crude oil production rate of 75,000 bbl/day which is one half of the average daily production based on the OTA estimate of 1.1×10^9 bbl produced from fireflooding over the next 20 years (Ref. 21).

The final column in Table 5-2 is a listing of the total emissions from Kern and Monterey Counties from TEOR operations in 1977 and 1978 assuming no controls. To distribute these estimated emissions between Kern and Monterey Counties, as indicated in the footnote on Table 5-2, the emissions in the final column should be proportioned 93 percent in Kern County and 7 percent in Monterey County. This distribution goes back to Table 5-1 where the distribution of TEOR fuel consumption between Kern and Monterey Counties was 138,000 to 10,000 bbl/day.

TABLE 5-2. ESTIMATED AVERAGE UNCONTROLLED DAILY EMISSIONS FROM TEOR OPERATIONS FROM KERN AND MONTEREY COUNTIES, TONS/DAY*

(Column No.) Pollutant	(1) Steam Gen. Alone Based on Crude Burned 1977-78	(2) ARB Est. Kern Co. for 1982 (Ref. 29)	(3) West Kern Co. SAI Estimate as of 7-78 (Ref. 20)	(4) SAI Est. Proportioned for Kern & Monterey Co. in 1978	(5) Steamflood TEOR Based in Crude Produced in 1977-78	(6) Fireflood TEOR Based on OTA Est. of Crude Production 1977-78	Total TEOR Emission# (5) + (6) 1977-78
Particulates							
. Total	37	21	16	37	68	6	74
. Solid only (i.e., front end)	24	-			24 †		24
. Condensible HC	0	0			14	6	20
HC (non-condensible)	2	2	4	9	1	10	11
Total HC (i.e., cond + non-cond)	2	2	4	9	15	15	30
SOx as SO_2	300	250	147	340	280	1	280
NOx as NO_2	83	184	85	200	68	2	70
CO	9	-	1	2	11	0.5	12
H_2S	0	-	-	-	0.05	0.01	0.06

* Based on operating at 85% of rated load, 80% of the time
† Same as for steam generators alone
§ Average fuel sulfur 1.2%
\# To proportion emissions between Kern and Monterey Counties the ratio is 0.93 for Kern to 0.07 for Monterey based on the distribution in Table 5-1

The growth of uncontrolled emission will follow the production forecast shown in Figure 5-1. Since the emissions listed for 1977-78 (Columns 1, 5, 6 and 7 of Table 5-2) are based on 230,000 bbl/day production, the uncontrolled emissions for any later date can be obtained by taking the predicted production rate from Figure 5-1 for the date in question and multiplying the emission rates in Table 5-2 by the ratio of the new production rate to 230,000 bbl/yr.

Substantial controls are being applied to these emissions as the result of various regulatory actions. It was beyond the scope of this contract to assess the impact of these controls on the emissions.

SECTION 6.0

EMISSION CONTROLS

Until recently, the TEOR operations ran with relatively little controls placed on air emissions. In Monterey County's San Ardo field, the operators were required to install SO_2 scrubbers a few years ago. In other locations, primarily Kern County, a few producers had installed sulfur scrubbers on steam generators and hydrocarbon collection systems on the well vents. This was the extent of controls until approximately the beginning of 1978. After that, because of the desire of the desire of the producers to expand the TEOR operations and the action of the regulatory agencies (EPA, ARB, and APCD) to limit further emission, the oil producers have begun controlling their emissions with combustion modification and add-on devices. In this section, we will review the various methods for emission control.

6.1 NITROGEN OXIDES

Nitrogen oxide emissions are generated by the oil field steam generators and air compressors used for steamflooding and fireflooding respectively.

6.1.1 Steam Generators

The steam generators are single burner, packaged boilers which operate at nearly constant load with mechanical linkages setting the air/fuel ratio which is typically set for an excess O_2 level of 3 to 7%. On many units by simply adjusting the excess O_2 level, the NO emissions can be reduced from 30 to 60%. Figures 4-2 and 4-3 illustrate this effect by showing the NO reduction as a function of excess O_2 level. On these same curves, the CO emissions are also plotted. As noted earlier, at San Ardo (Figure 4-2) as the O_2 level is reduced, the CO remains constant until a threshold level is reached and then it begins to rise dramatically. This point of CO rise is essentially the lowest level of O_2 on which the burner can effectively operate. There is another factor that can limit the reduction in excess O_2. As the excess O_2 is lowered, the appearance of smoke in the stack gas sometimes occurs before the CO rise begins as it did at Tenneco (Figure 4-3). Therefore, the minimum O_2 is determined by either the smoke or CO rise effects. For oil firing the smoke limit is more often reached before the CO limit because of localized fuel rich areas in the combustion zone which are created as the O_2 level is reduced. At San Ardo, if smoke occurred before the CO rise, the smoke was removed by the SO_x scrubber on that unit.

The actual NO emission reduction possible is dependent on the specific unit and can vary from 25 to 60%. The reduction in O_2 not only is beneficial in reducing emissions but also improves the unit's fuel efficiency. The problem with operating these units at the minimum O_2 levels is discussed in Section 4.3.1.

Certain burner improvements can be made which can reduce the excess O_2 level at which the smoke or CO become objectionable. In fact, there are on the market "Low Excess Air" (LEA) burners which allow a unit to run at excess O_2 level less than 1% with a consequential efficiency improvement. These burners are generally not effective in lowering NO emissions because, while the excess O_2 is lowered, the fuel/air mixing action is so intense that the combustion reaction time is shortened and the combustion efficiency is improved. This improved combustion, while fuel efficient, creates a higher flame temperature and phenomenologically produces a high NO concentration in the exhaust gases. Robinson (Ref. 1) reports baseline emissions from a 50×10^6 Btu/hr with the original standard burner and with an LEA burner both manufactured by the same burner company. At 4% excess O_2, the NO_x concentrations ranged from 275 to 310 ppm for the standard burner at various loads and 500 to 575 ppm for the LEA burner at the same load range. For this LEA burner at 1.0% excess O_2, the NO_x emissions were reported at a value of approximately 400 ppm, still much higher than for the standard burner where (although there are no data reported to this effect) the NO_x could probably be reduced to 175 or 200 ppm.

Several manufacturers--CEA Combustion Inc., Coen Co., Process Combustion Corp. (PCC), TRW, and John Zink--make low NO_x burners that they claim will produce substantial reductions in NO_x emissions. John Zink offers a low-NO_x steam generator (Ref. 33). Generally, these units feature staged combustion

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where the fuel is first reacted with less than the stoichiometric amount of air, then the gases are cooled by passing them over water/steam tube and finally the secondary air is added in the furnace. Flue gas is recirculated to mix with the combustion air in either or both the primary or secondary flame zones. Claims for these devices range from 250 ppm down to 150 ppm or lower. At the present time, however, there are very little data on which to evaluate the effectiveness of these units on steam generators.

In testimony to the ARB, Holliday (Ref. 34) presented unreferenced data for the PCC, Zink, and TRW burners on 50 million BTU/hour steam generators. These data are presented in Figure 6-1. The TRW burner was tested on a Chevron unit and the PCC and Zink burners were tested on a Grace Oil Co. unit. These low NO_x burner data are compared to other date (also unreferenced) for a conventional burner also shown on Figure 6-1. All of the low NO_x burner emissions data fall within the one-standard-deviation band for the conventional burner except for a few points at high O_2 levels which are above the conventional burner band.

Although the existing data seem to indicate that low NO_x burners may reduce NO_x at low excess air levels, more research is required before a conclusion is reached. Each burner characterized was tested on a different unit with different fuel properties, loads etc. The conventional burner may have been tested under more favorable conditions than those for the low NO_x burners. More evaluation is required comparing emissions from conventional and low NO_x burners on the same unit under the same conditions.

If these units are shown to be effective, the estimated retrofit cost is between \$50,000 and \$75,000 plus the cost of an O_2 trim system to permit the unit to operate with the lowest possible O_2 level.

Other techniques to reduce NO_x emission besides lowering O_2 and using new low NO_x burners are to:

a. Modify the unit for staged combustion and exhaust gas recirculation

b. Inject ammonia into the exhaust gas
   - without catalyst (Exxon's Thermal $DeNO_x$)
   - with catalyst

c. Combinations of the above

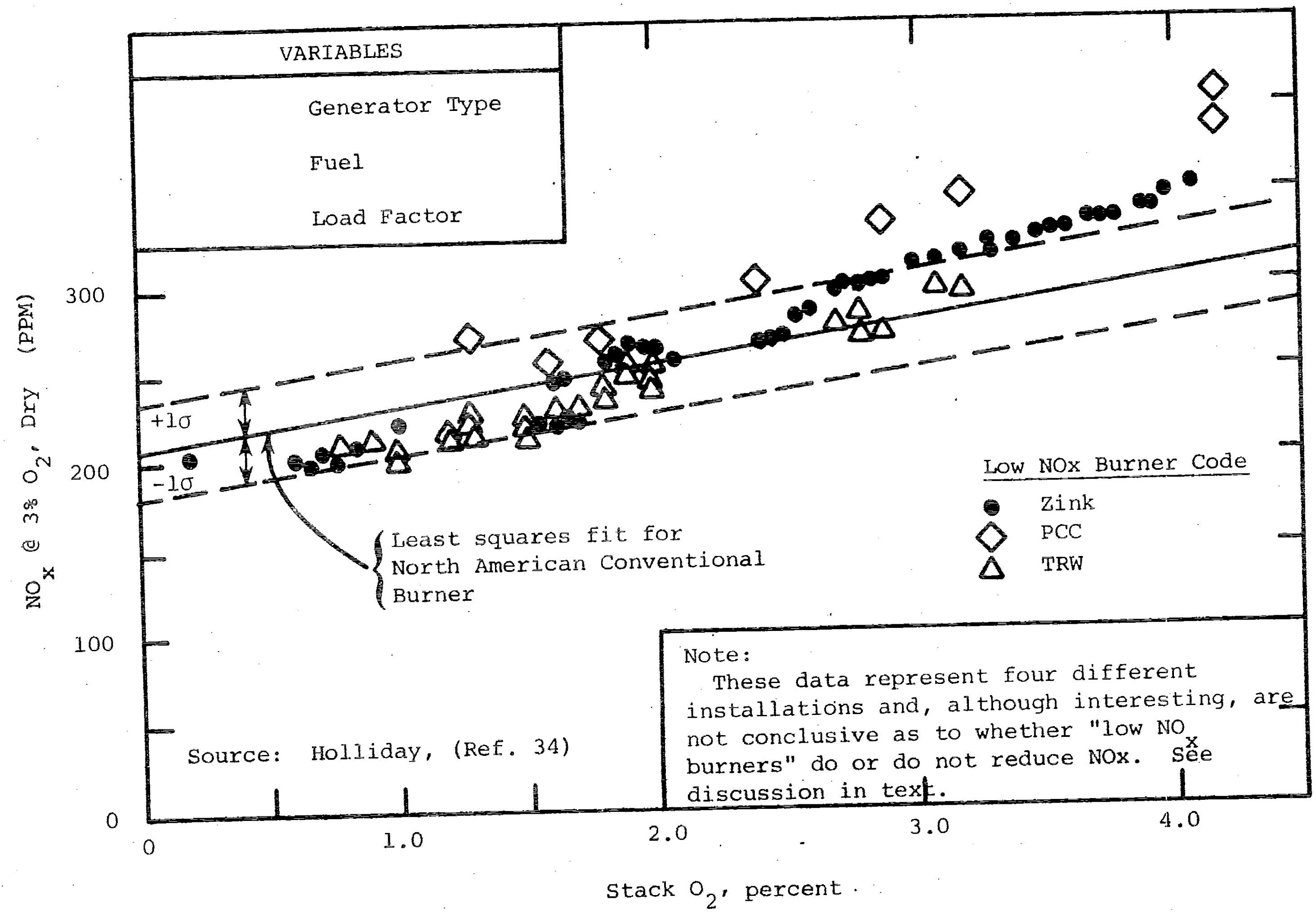

Figure 6-1. NO_x emission data for three "low NO_x burners" plotted against a one standard deviation (σ) range of the NO_x emissions from conventional burners

Staged combustion, as in the low NO_x burners, involves stretching out the flame zone by burning fuel rich at the burner tip and continuously adding air downstream (referred to as overfired air). Along with excess O_2 reduction, this technique may reduce NO_x from 30 to 70% depending on specific conditions. To our knowledge, this technique has not been tried on a steam generator. The EPA has sponsored a similar development by KVB for single-burner process heaters in which overfired air is introduced into the exhaust stream of a fuel rich burner. The results showed NO_x reductions of over 50% on the process heaters. A modification of this sort could run from $10,000 to $15,000.

Exhaust gas recirculation with reduced O_2 can produce the same range of reductions as staged combustion (40 to 70%). Again we are unaware of any work to develop a retrofit technique for steam generators although it is a well-developed technique for utility boiler applications. The new zinc steam generators, mentioned above, incorporates this technique. This retrofit might cost more like $30,000 to $40,000 to modify a unit because it would require the acquisition of a high temperature fan to circulate the hot exhaust gases.

Thermal $DeNo_x$ is another NO_x control technology that may prove to be effective for steam generators. The process, patented by Exxon Research & Engineering (ERE) (U. S. Patent 3,900,554) involves the introduction of ammonia at one to two mols per mol of NO_x and at a temperature between 1700° and 1800°F (Ref. 1). In this temperature range the ammonia reacts homogeneously (i.e., without catalyst) to reduce NO_x to nitrogen and water. Hydrogen can be added with the ammonia to reduce the reactive temperature range, but this is probably not required for the oil field steam generators. The process requirements are to efficiently mix ammonia with the gas stream in the desirable temperature range and provide adequate residence time for the reaction. The practical difficulty sometimes encountered with injecting in the right temperature range is the stability of the temperature profile within the boiler as a function of operating variables such as fraction of rated load, excess air, etc. Since oil field steam generators are typically not load-following boilers, this application should be minimally affected by such problems. Injection and mixing requirements are determined according to ERE proprietary technology which includes the demand for either compressed air or steam as a carrier for the ammonia. The latter is probably the more convenient for oil field operation. Sufficient reaction time and practical injection location depend on the boiler design and cannot be generalized with regard to the population of boilers now in the field.

NO_x reductions as high as 95% have been achieved in the laboratory under controlled conditions (Ref. 1), but in field applications the variations from ideal temperature time and mixing conditions have caused the process to yield reductions in the range of 40 to 70%. To date, Thermal $DeNO_x$ has been tested on oil field steam generators in two test series, one at CWOD and the other at Getty. The CWOD test series (Ref. 1), data were obtained during short term tests on a 50 million BTU/hr Struthers Thermoflood steam generator operating on approximately 0.7% N oil. Tests with a conventional burner yielded NO_x values of 250-300 ppm without ammonia injection and values ot 80 to 125 ppm with ammonia injected at 1.0 to 1.5 mols per mol of NO_x, reductions in the range of 50 to 73 percent. With a North American low excess air burner operating with 0.5 to 1% excess O_2, initial uncontrolled NO_x levels were about 400-450 ppm. With ammonia injection at 1.3 to 2.0 mols per mol NO_x yielding reductions of 70 to 82%, levels of 80 to 120 ppm were achieved.

Tests conducted by Getty Oil utilized the principles of the Exxon process, but did not make use of the Exxon proprietary technology. In limited testing in a 50 MMB/hr steam generator, burning 0.9% N residual fuel, NO_x reductions of 50 to 70% were achieved starting with uncontrolled emissions of about 314 ppm and injecting at about 1.5 to 3.0 mols per mol of NO_x (Ref. 38).

These results, while promising, are difficult to extrapolate to the whole steam generator population and to long term operation. For example, the long term stability of the temperature profile with increasing deposits on heat transfer surfaces is not known, nor is the long-term effect of possible deposits of salts such as ammonium bisulfate that may result from reactions with SO_3 and residual ammonia.

The cost of a Thermal $DeNO_x$ installation will depend on the number of nearby steam generators that can share the components such as ammonia storage and feed system. Assuming a cluster of six 50 million BTU/hr steam generators, a system will cost somewhere in the range of \$320K to \$620K (including Exxon royalty) depending on the extent of system automation and redundancy and distance separating the units. This corresponds to vendor battery-limits costs* in the range from \$11 to \$22 KW. Assuming total project costs to the owners of 1.5 to 2 times vendor battery-limits costs (to account for such things as project engineering, construction supervision, startup, performance testing, contingencies, etc), total project costs could run in the range of \$17 to \$44/KW. Ammonia is available at from 10 to 20 cents/lb depending on quantity delivered and remoteness from sources of supply. For example, a 50 MMB/hr steam generator operating at 300 ppm NO_x as NO_2, to be controlled 60% by ammonia injection at 1.5 mols NH_3 per mol NO_2 would require about 11 lb/hr ammonia which would cost between \$10,000 and \$20,000 per year. Other operating costs would include the steam for dilution of ammonia plus operations and maintenance costs that would be a tradeoff with initial capital costs. Total operating cost would be expected to run about \$200,000 to \$250,000/yr for the 300 million BTU/hr cluster assuming 16% per year debt service.

Selective catalytic reaction (SCR) of ammonia with oxides of nitrogen to produce water and nitrogen has been long known and has patents dating back to before 1961. Recently, more interest in reducing oxides of nitrogen emissions by stack gas treatment has resulted in numerous modifications of the basic process to improve efficiency, catalyst life, cost, and suitability to dirty gases. A recent EPA technology survey listed 22 SCR projects in various stages of development from bench scale to commercial plant demonstration (Ref. 35). All but four of these are Japanese.

Nearly all these processes have common features. The flue gases are drawn off the unit, where the gases are between 480° and 750°F, and are ducted to a reactor containing a proprietary catalyst. (Catalyst materials include platinum, copper sulfate, titanium oxides, vanadium oxides, and other active metal oxides and sulfates.) Before reaching the catalyst, ammonia is injected into the gas stream as uniformly as possible in a ratio of about 1.0 to 1.5 mols of ammonia per mol of NO_x in the flue gas. The catalyst volume is sized to provide a residence time of somewhere between one second and one-third

*Battery limits costs includes all equipment supplied by the vendor, installation, unit modification and utilities hookups. Not included are the additional user indirect investment and capital charges, e.g., engineering design and supervision, A&E contractor, construction expense, etc. Other definitions of battery limits costs defined this as whatever the user lists in the specification to the vendor. For example, the user may furnish the fan motor in order to match his electrical system.

second (corresponding to space velocities of 3600/hr to 10,000/hr, respectively). During that time, the ammonia selectively reacts with the oxides to nitrogen to reduce NO_x emission by 80% to 95%.

The pressure drop in the ducting and flow through the reactor ranges from a few inches of water to as much as 30 inches of water depending on the catalyst type, configuration, and time on-stream. This will require an extra boost fan for most units.

With time, the catalyst performance degrades from its initial activity due to poisoning or coating of the catalyst with particulate material such as fly ash or sulfates created by the reaction of ammonia and SO_3. Typically, the more active catalysts, such as those of noble metal, require the least reaction volume but tend to degrade the fastest. One such degradation mechanism involves SO_3 attack of the substrate on which the catalyst metal is deposited. The key operational questions concern the rate of degradation and whether catalyst cleaning or replacement is required. These questions bear very heavily on the process economics. The most sensitive parameters affecting degradation are the sulfur oxides, particulate concentrations, and particulate physical characteristics in the flue gas. For flue gases from the burning of natural gas or LPG, the catalyst lifetime may reach five years; but for flue gases from the burning of high sulfur fuel oil or coal, the catalyst lifetime may be less than a year. For applications with such dirty gases, particulates and/or sulfur oxides removal systems may be incorporated. Such flue gas conditioning complicates the overall system; and where substantial reheat is required after a wet scrubber removal of sulfur oxides, there is considerable loss in unit efficiency.

Of the various catalyst bed configurations the one that seems to be the most favored for coal and heavy residual oil fired applications is the parallel flow configuration. It has the lowest pressure drop, is least likely to become plugged by particulate deposits, and is the most adaptable to some form of on-line particulate removal such as soot blowing. In a recent EPA survey (Ref. 36) a total of three completed parallel flow SCR installations on low sulfur residual oil fired industrial boilers was listed. All were in Japan. No such installations have thus far been completed in the United States to the author's knowledge. These projects ranged in flow capacity from about 100,000 SCFM to about 125,000 SCFM, corresponding to heat input ratings from about 500 million BTU/hr to 600 million BTU/hr. Installation completion dates ranged from January 1978 to April 1978. Two residual oil fired utility boiler installations were also listed, one at 22,000 SCFM and the other at 1,080,000 SCFM. (Two additional installations of about 1 million SCFM are scheduled for 1980 and 1981.) Because of the short time that these projects have been in operation, it has not been possible to accumulate substantial catalyst life data. Most catalyst system cost analyses for residual oil fired units are based on either one or two years of catalyst life. It is difficult to predict the catalyst life in an oil field stream generator burning field crude oil.

Other catalyst configurations, such as moving beds and packed beds, have also been tried with varying degrees of success on heavy oil fired boilers. In an overall evaluation of these against the parallel flow configuration, EPA ranked them lower by considering such factors as performance, cost, energy requirements, reliability, and development status (Ref. 36). Hence the discussion is focused on the parallel flow configuration for the TEOR application.

Costs for parallel flow SCR systems have been estimated for residual fuel oil service in the EPA survey (Ref. 36) at the 30 million BTU/hr and 150 million BTU/hr size operating with 90% NO_x reduction starting from 430 ppm and 300 ppm, respectively, 5000/hr space velocity. Costs were estimated for original equipment installation with a consistent set of cost elements and cost factors, including complete system costs both direct and indirect. They were stated to be ± 50% accurate estimates. In the system used to generate the estimate, vendor battery-limit capital cost was about half of total capital costs. At the 30 million Btu/hr scale, total capital cost was about $200 K (1978) or about $67/KW. At the 150 million Btu/hr scale, the capital cost was about $500 K (1978) or about $33/KW. Annual operating costs were $108 K and $223 K, respectively, based on a 0.6 capacity factor and about 15% annual capital cost, and one-year catalyst life.

The only specific manufacturer-provided system cost presented in Ref. 36 was for a new 620 million BTU/hr oil-fired unit, 90% NO_x reduction from 150 ppm using a reactor with 4000/hr space velocity. The capital costs cited, presumed to be vendor costs, were about $1,300 K (1977) or about $21/KW. On the basis of vendor costs being about half of total project cost to the owner, total capital cost would be about $40/KW. Scaled down to 150 million BTU/hr using the 0.6 power scaling rule (e.g., see Ref. 36), the total project cost for that size unit would be about $70/KW, about twice that estimated using the generalized costing approach of Ref. 35.

Vendor quoted costs for new installations were reported by Ando (Ref. 37) for SCR systems down to 13 MW (about 130 million BTU/hr) based on Mitsui Shipbuilding data. Capital cost for the system was reported at $765 K or $59/KW in 1977 dollars. Costs submitted to the Japanese Environmental Agency from five vendors agreed with the Misui data within about ± 30% (Ref. 37). Ando estimates total owner cost to be about 1.5 times vendor battery-limit cost, corresponding to $88/KW for 130 million BTU/hr or $83/KW for 150 million BTU/hr.

As in the case of Thermal DeNO$_x$, SCR systems for clustered units sharing a common ammonia storage and feed systems would cost less than stand-alone units.

6.1.2 Compressors

The compressors used for fireflooding air injection are driven by internal combustion engines usually four-cycle, spark ignition types, usually fired with natural gas although some gasoline and diesel may be used.

The approaches to NO$_x$ control in stationary, reciprocating engines can be classified as either (1) engine modifications or (2) exhaust gas treatment. The engine modifications can be further divided into techniques which require engine hardware changes or those which only require changes to the operating conditions. Examples of these emission control techniques are shown in Table 6-1. These are discussed in more detail in the following sections.

TABLE 6-1. EMISSION CONTROL METHODS FOR RECIPROCATING ENGINES

EMISSION CONTROL METHODS FOR RECIPROCATING ENGINES

	Applicable to	
	Spark Ignited	Compression Ignition
A. Engine Modification		
1. Operating Conditions		
Speed	X	X
Load	X	X
Air/Fuel Ratio	X	
Ignition Timing	X	
Fuel Injection Timing		X
Air Temperature	X	X
Air Pressure	X	X
Exhaust Back Pressure	X	X
2. Engine Hardware		
Exhaust Gas Recirculation	X	X
Water Injection		
manifold	X	X
fuel/water emulsion		X
Valve Timing	X	X
Compression Ratio	X	X
Combustion Chamber-Stratified Charge	X	
Fuel Injection Schedule		X
Fuel Injector Design		X
H_2 Enrichment	X	
B. Exhaust Treatment		
1. Exhaust Thermal Reactors	X	
2. Catalytic Converters		
a. Oxidation (CO/UHC)	X	X
b. Reduction (NOx)	X	

A. Operational Changes--

1. Air Fuel Ratio--The air/fuel ratio of a spark-ignition engine has a dramatic effect on the NO_x emissions as shown in Figure 6-2. Adjusting the air/fuel ratio to the fuel-rich engine results in lowered NO_x emissions at the expense of increased unburned hydrocarbons, and carbon monoxide emissions along with increased fuel consumption. In gasoline fueled engines, adjustment of the air/fuel ratio to the fuel-lean region is limited to slightly leaner than stoichiometric. With further leaning of the mixture, which should result in substantial reductions in NO, CO and unburned hydrocarbons, engine misfire results. Operating at very lean air/fuel ratios appears to require fuel stratification, improved carburetion of fuel injection. Another technique is to use hydrogen enrichment to extend the lean limit.

2. Ignition Timing--The ignition timing can have an effect on the NO_x emissions from spark ignition engines, with retarded firing producing moderate reductions in NO_x emissions. As the timing is retarded, a larger fraction of the combustion occurs during the expansion stroke resulting in a decrease in the peak cycle temperature and thus the formation of nitric oxide. This is illustrated in Figure 6-3. However, these reductions in NO_x emissions are also accompanied by a loss in both engine power and fuel economy and at high loads can cause overheating (Ref. 22). Results of timing variations on a Cooper-Bessemer GMVA-8 2-stroke spark gas engine (1080 hp, 300 RPM) are shown in Figure 6-3.

3. Engine Speed--The effect of engine speed on NO_x emissions is not well documented and understood. Nebel and Jackson (1957) (Ref.23) found NO_x emissions to increase with engine speed for rich mixtures and decrease with engine speed for lean mixtures. These effects are not associated directly with the engine speed but rather to changes in charge dilution by the residual gases as a result of the change in engine speed (Ref 24).

The effect of engine speed on the large Cooper Bessemer GMVA-8 engine are presented in Figure 6-4 where the NO_x emissions decrease substantially as the engine speed was increased from 275 to 400 RPM. Again, this appears not to be a direct influence of the engine speed but rather of a change in air/fuel ratio.

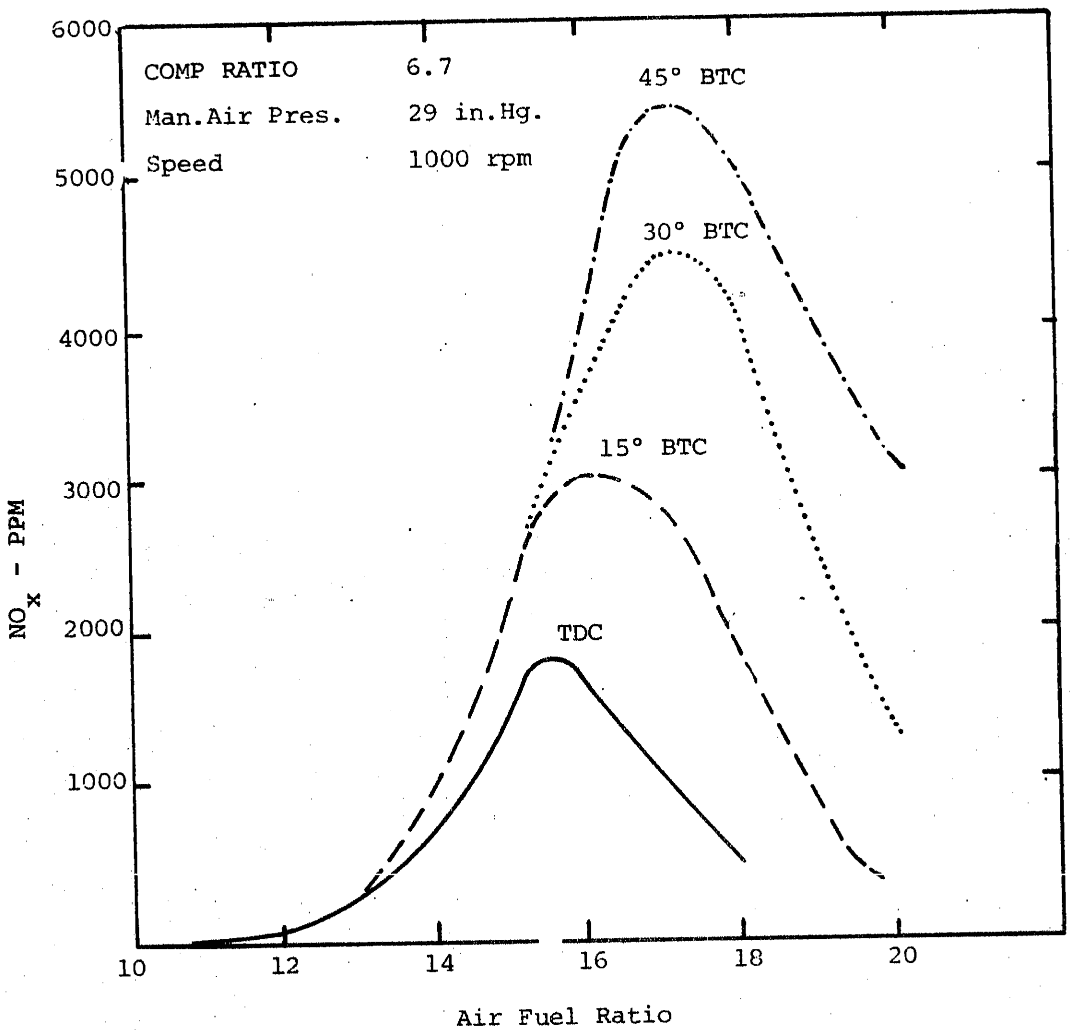

Figure 6-2. Effect of air-fuel ratio and of ignition timing on oxides of nitrogen.

KVB 5807-842

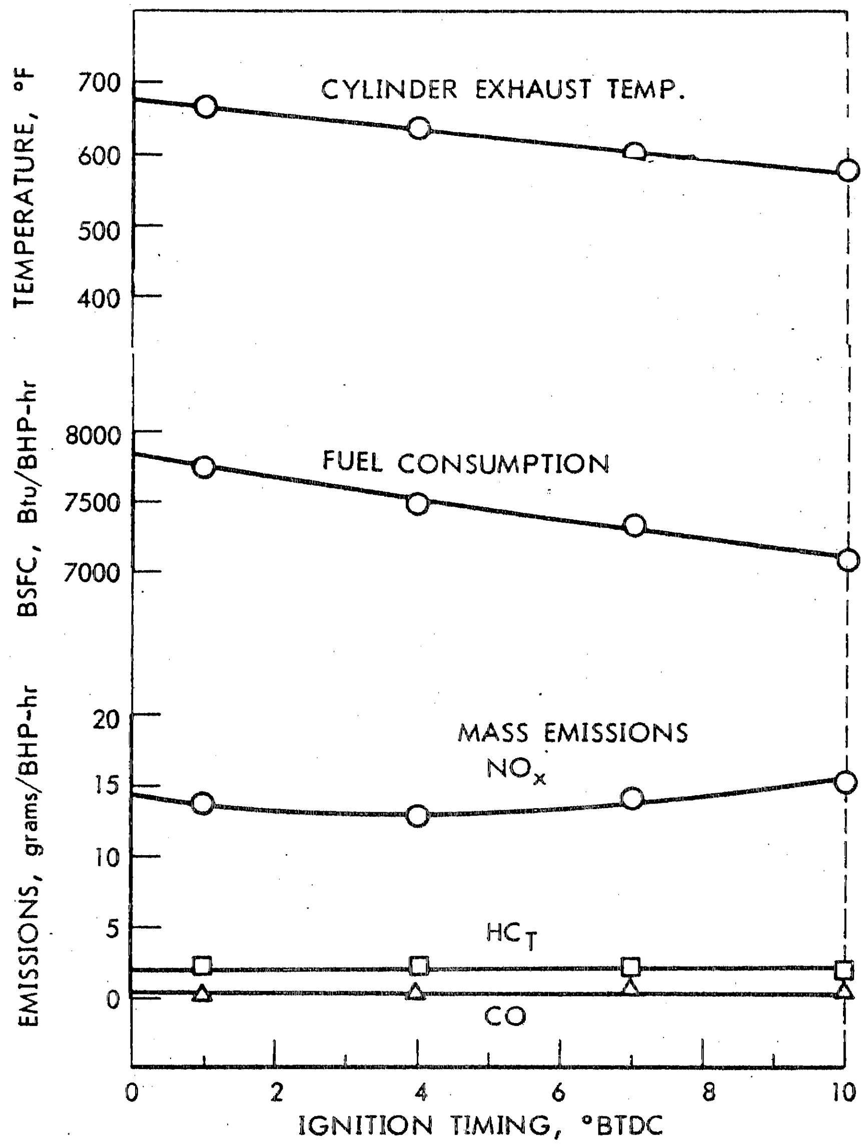

Figure 6-3. Cooper-Bessemer GMVA-8 2-stroke atmospheric spark engine 1080 BHP at 300 RPM, 82.5 BMEP, base conditions. (Ref. 22)

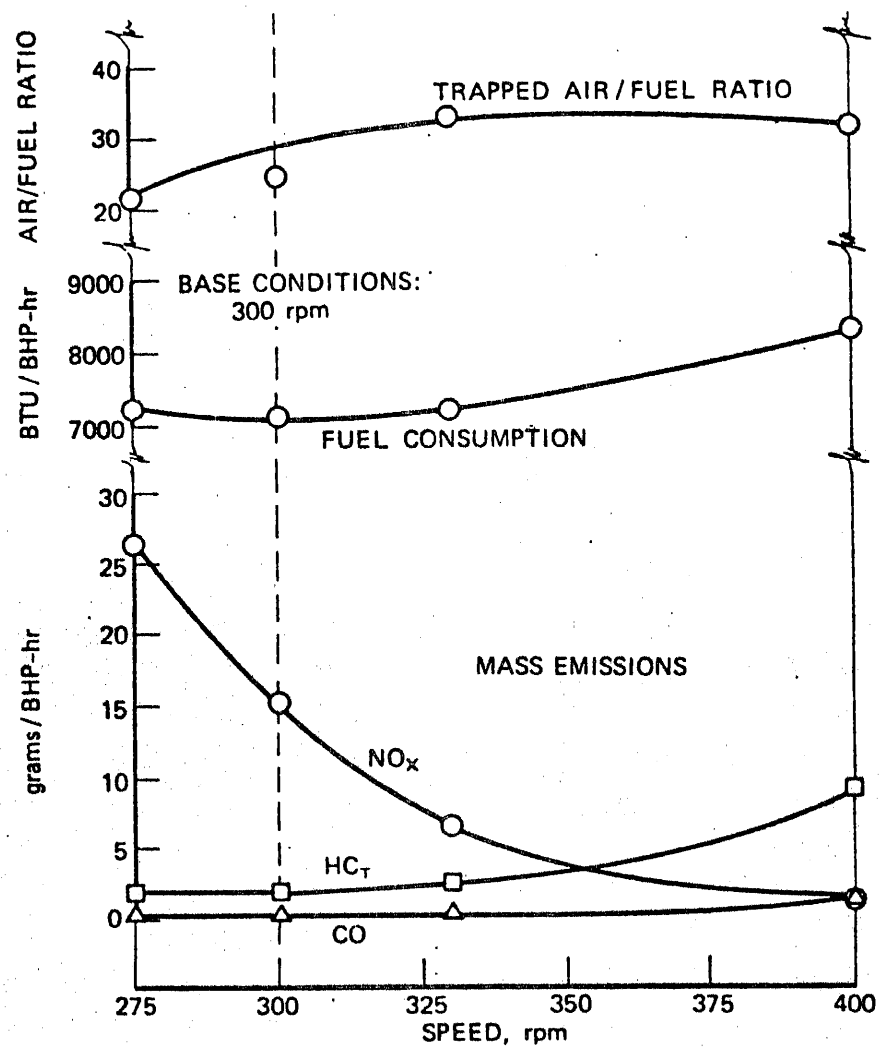

Figure 6-4. Cooper Bessemer GMVA-8 2-stroke atmospheric spark-gas engine power output 1080 BHP, base conditions.

6.1.3 Intake Charge Temperature

Reducing the temperature of the fuel/air mixture results in a decrease in NO emissions and also in the specific fuel consumption. This is shown in Figure 6-5 for the Cooper Bessemer engine referred to above. The temperature reduction can be accomplished by eliminating manifold heating or by utilizing an evaporative cooler. The evaporative cooler would provide a further NO_x reduction due to the humidification of the combustion air.

6.1.4 Exhaust Gas Recirculation

Adding exhaust gas recirculation to the charge acts as a diluent to reduce the peak combustion temperatures reached in the chamber. Since the NO_x formation depends exponentially on temperature, even relatively small reductions in temperature can have a large effect on the NO_x formation. Forty to eighty percent reductions in NO_x can be achieved with only moderate amounts of recycle (10 to 20%). This is shown for a number of gasoline fuel engines in Figure 6-6. With larger amounts of recycle, the effectiveness is diminished. The NO_x reductions with recycle are not without tradeoffs in that the dilution by the recycled gas results in a loss in power which translates directly into a fuel economy penalty. Also, little information is available on the effect of exhaust gas recycle on engine life which is an important aspect for a stationary engine with an expected life of about 30 years.

6.1.5 Water Injection

Water injection into the intake air or directly into the cylinder can also be used to reduce NO_x emissions. The latent heat of vaporization reduces the temperature of the mixture and changes the specific heat of the mixture to reduce peak temperatures. NO_x reductions on the order of 80% can be achieved with water injection on the order of one pound of water for each pound of fuel burned. This is illustrated in Figure 6-7, for water injection into a 4-cycle naturally-aspirated, spark ignition gas engine. The increased CO and hydrocarbon emissions with increased water injection may be due to quenching as a result of poor water distribution in the cylinder. Just as with exhaust gas recirculation, before

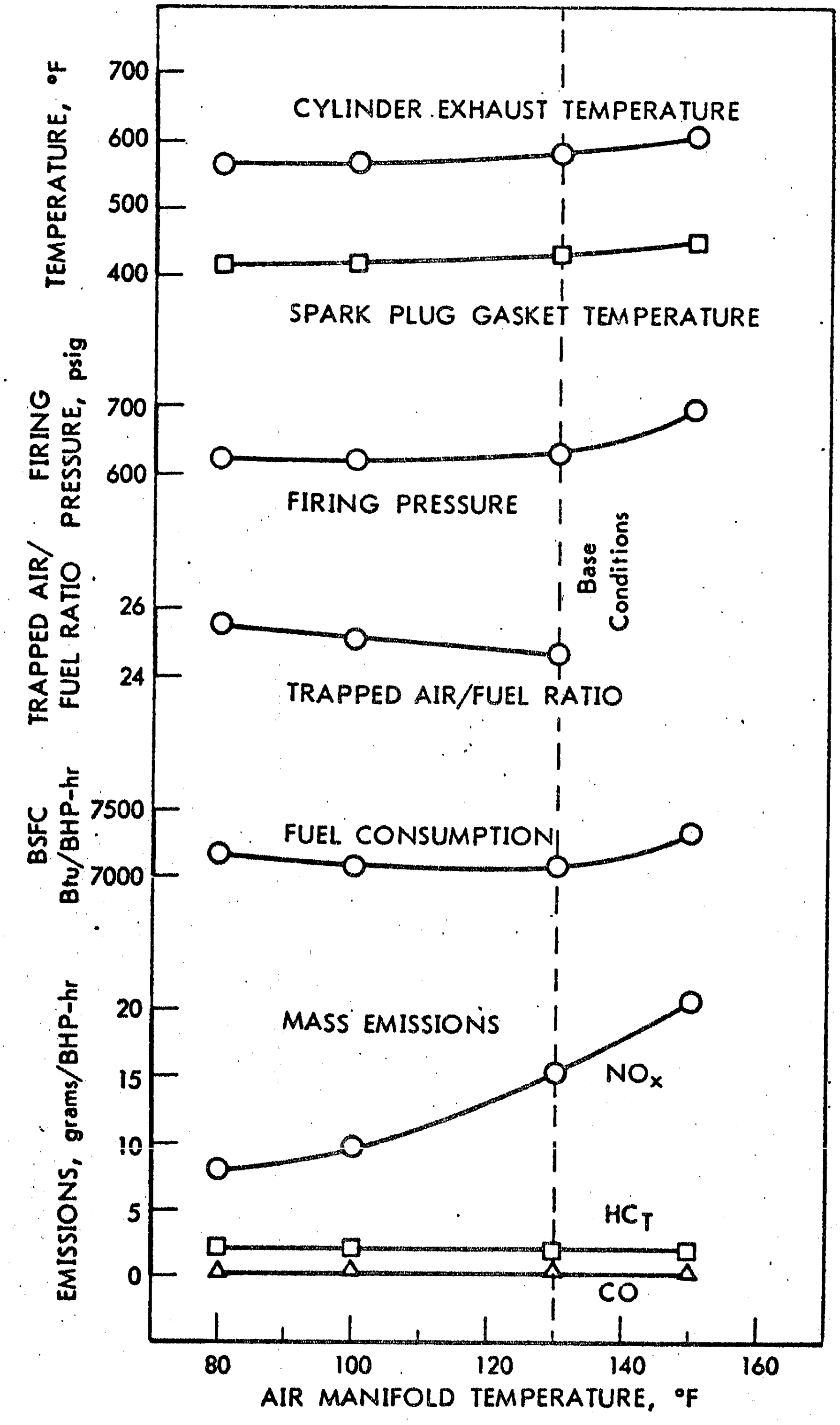

Figure 6-5. Effect of air manifold temperature, Cooper Bessemer GMVA 8-2 2-stroke, atmospheric spark-gas engine 1080 BHP at 330 RPM, 82.5 BMEP, base conditions.

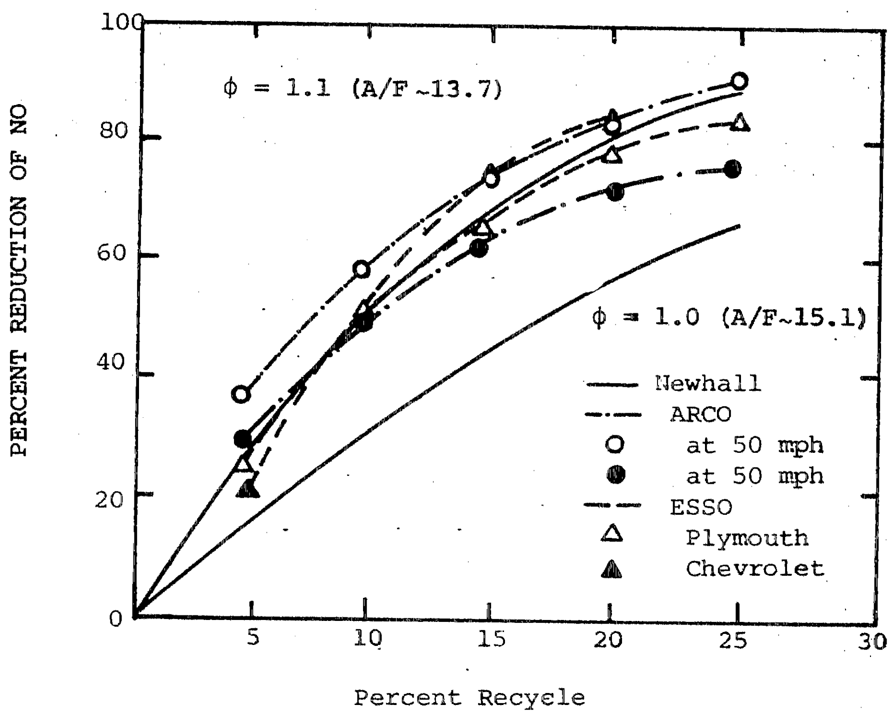

Figure 6-6 (a). Effect of EGR on NO reduction.

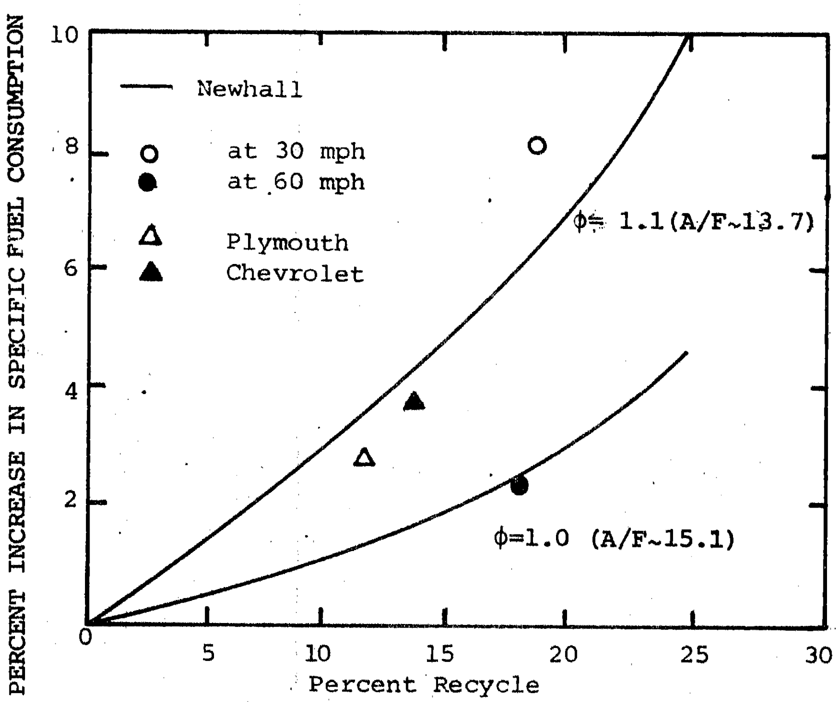

Figure 6-6 (b). Effect of EGR on specific fuel consumption.

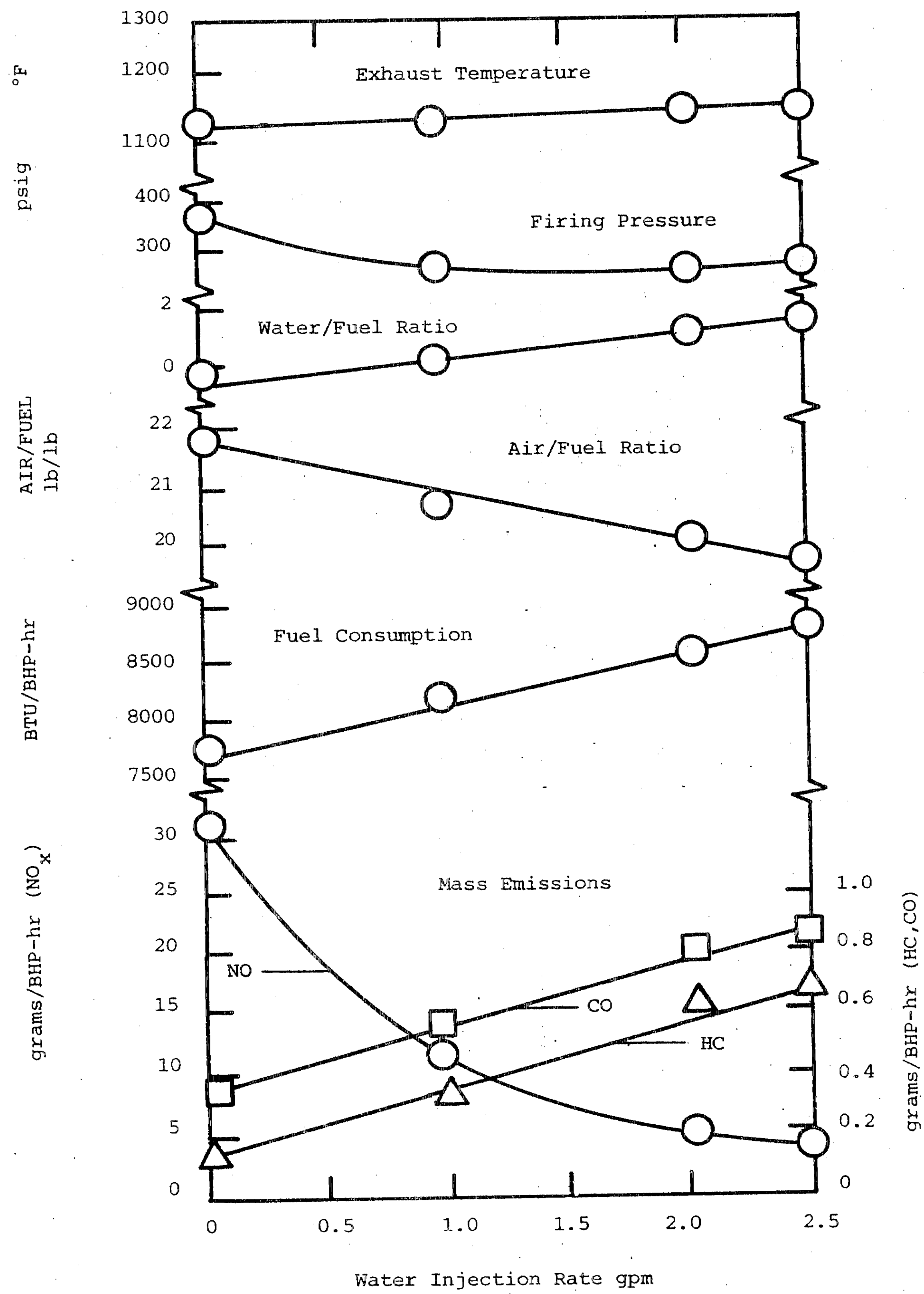

Figure 6-7. Effect of water injection on emissions and performance - Ingersol-Rand, PKVGR-12, 4-cycle naturally aspirated spark-gas engine.

water injection can be applied in the field, the long-term effects on lubricating oil and engine life should be investigated.

6.1.6 H_2 Enrichment

Another potential method for controlling NO_x emissions is to extend the lean operating limit by enriching the fuel/air mixture with small amounts of hydrogen. Very little information is available as to the applicability of applying this technique to stationary reciprocating engines.

6.2 SULFUR OXIDES

The only methods of reducing SO_x emissions are to either reduce the fuel sulfur or to use a flue gas desulfurization (FGD) systems. FGD systems are available in varying degrees of effectiveness and cost. The simple water scrubbers used in Mobil's San Ardo fields employ the connate water, that is pumped from the wells, to scrub the exhaust gases. This water contains various calcium salts and other minerals that react with the SO_2 and SO_3 in the exhaust stream to form sulfates and sulfites which precipitate out and are pumped back into the wells. The efficiency of the unit as measured on this program was 80%. Other scrubbers use such chemicals as lime, limestone, ammonia and amines.

Our investigations reveal that the simple water scrubbers tested at Mobil San Ardo (see Figures 3-2 and 3-3) cost approximately $65,000 in 1970. Mobil estimated that they might be over $100,000 today. One manufacturer (Ref. 26) provided information on two sophisticated scrubbers. One unit was a lime/limestone, combined SO_x and particulates scrubber with efficiency of 95% or greater on both pollutants. This company also has a less sophisticated unit which will provide 90-95% sulfur reduction but only 50 to 70% particulates reduction. They estimated the cost for these two scrubber type installed on a manifolded cluster of six 50-million Btu/hr units at a turnkey price of approximately $1.2 and 1.0 million respectively. Chemical Engineering (Ref. 27) indicated a cost of $300,000 to $500,000 for a

50×10^6 Btu/hr size unit. So the range of scrubber prices is approximately ten to one depending on the degree of recovery required. Annual operating costs exclusive of debt service are estimated at 2 to 4% of the capital cost, one-third of which is for chemicals.

An emerging method of FGD is to inject chemicals into the gas stream in the form of dry powders (referred to as dry alkali systems) or slurries (referred to as spray dry systems). The dry alkali system uses commercial chemicals such as Nahcolite (primarily sodium bicarbonate) or Trona (a mixture of sodium bicarbonate and sodium carbonate). Reductions of the order of 70% are expected but the method is still in development. The spray dry system uses slurries of sodium or calcium salts, primarily the carbonates. These systems appear to have a potential for 80 or 90% reduction.

In both the wet and dry systems, the SO_2 is reacted in the gas stream to form solid sulfate and sulfite particulates which are removed by a baghouse or electrostatic precipitation (ESP). The baghouse seems to have a technical advantage in that the reaction with the SO_2 can occur not only in the gas stream but in the filter cake which forms on the bag surface.

These systems are too new for firm cost figures but should be similar to or possibly lower than wet scrubber costs. The SCAQMD (Ref. 28) compares wet scrubber costs at \$1,000/ton SO_2 removed to the dry alkali system at \$400 to \$1,200/ton SO_2 removed. The real cost advantage to these systems is that they serve a dual purpose of removing both SO_x and particulates. The disadvantage with these systems is the disposition of the spent material which must be land filled in dry isolation cells to prevent soluble material from leaching into underground water supplies.

6.3 PARTICULATES

Particulates control for TEOR operations is primarily associated with the steam generator exhaust emissions. The particulate material from well vents is primarily condensible hydrocarbons which will be covered in the next section.

The particulates in the oil fuel combustion exhaust of an oil field steam generator may be removed by a baghouse, a wet scrubber or an electrostatic percipitator. Since SO_2 reduction is a more serious problem with this source type, it is desirable to combine particulate and SO_2 removal into one system.

Wet, dry or slurry scrubber systems are potential candidates for this application which must be evaluated.

The newest overall systems for combined SO_2 and particulate removal are the dry alkali or spray dry systems employing a baghouse. These would not only provide 70 to 90% SO_2 removal as discussed above, but would remove better than 95% of the particulate matter. This approach has some apparent cost advantage but is new and has no field service on which to base a reliability estimate.

The wet scrubber is a proven method for both SO_x and particulates control. However, the system must be designed for the dual purpose. The simple water spray scrubber tested in Mobil San Ardo provided approximately 95% removal. As mentioned before, the cost will vary with performance requirements.

6.4 HYDROCARBONS

The only hydrocarbon emissions that can be controlled (other than by assuring that the combustion processes are properly tuned) are those from the well vents. The well vent emissions are 98% steam and the remainder are hydrocarbons, primarily condensible in the case of steamflooding and a mixture of condensible and non-condensible in the case of fireflooding.

To control the hydrocarbon emissions, two steps are required. The first step is condensing the steam and condensible hydrocarbons, decanting the hydrocarbons and recovering both the hot water and liquid hydrocarbons. The second step is to pass the escaping vapors through a charcoal absorption system or an incinerator to collect or destroy the non-condensible hydrocarbons. Right now many oil companies have vapor recovery systems which collect the condensible hydrocarbons and hot water while emitting water vapor and gaseous hydrocarbons. As stated above, for the steamflood this is effective in accounting for nearly a 99% recovery. For fireflooding this would only account for a 40% recovery.

To improve the fireflood recovery, an economic study should be made to compare the cost effectiveness of a flare system to a charcoal recovery system.

The reader is also reminded that the fireflood tests were few in number and may not be representative of the population. Therefore, before drawing any firm conclusions, some additional testing would be prudent.

6.5 CARBON MONOXIDE

The control of carbon monoxide is only feasible through proper burner maintenance and control. As shown in Figures 4-2 and 4-3, the CO levels are of the order of 50 ppm and are too low to be of concern.

6.6 ALTERNATIVE TEOR SYSTEMS

At this final point in the report and in conjunction with emission controls, it is appropriate to mention a relatively new TEOR approach which has both emissions reduction as well as energy saving potential.

This approach is sponsored by the Department of Energy at the Sandia Corporation, Albuquerque, NM. The project called "Deep Steam" involves the development of an underground steam generator, which is lowered to the bottom of the injection well where it is fed fuel, air and water and generates steam and combustion products which are released into the production zone. The concept is designed to service very deep wells and to avoid the energy lost as the steam travels down a long injection tube. In this concept, room temperature fuel oil (eventually the lease crude), water and air are pumped to the combustor where the fuel and air burn and generate steam in a direct contact heat exchange with the water.

The emissions advantage is that most of the combustion exhaust will be discharged deep underground which provides a natural means to scrub the combustion exhaust. The only combustion exhaust generated on the surface will be that from the internal combustion engines driving the pumps and compressors feeding the steam generators.

The Sandia Corporation is now developing this device and has been testing it in a Kern County location since late 1979.

REFERENCES

1. Robinson, J. M., "NOx Control by Thermal DeNOx Process and Tertiary Oil Recovery Steam Generator," Air Pollution Control Association Paper No. 79-33.4, presented at Cincinnati, OH, June 24-28, 1979.

2. Environmental Protection Agency, "Compilation of Air Pollutant Emission Factors," Publication AP-42, 3rd Edition with Supplements, August, 1977, Research Triangle Park, NC.

3. Taback, H. J., "California Thermal Oil Recovery Operations Emission Studies," Air Pollution Control Agency Paper No. 79-19.3, presented at Cincinnati, OH, June 24-28, 1979

4. Copyright, National Petroleum Council, 1976.

5. Leichnitz, Kurt, Detector Tube Handbook, August, 1976, Drägerwerk, AG, Lübeck, Federal Republic of Germany.

6. Kern County APCD Test Report, Belridge Unit No. 25, March 20, 1974.

7. Kern County APCD Test Report, Belridge Unit No. 25, April 11, 1974.

8. Kern County APCD Test Report, Chevron Unit No. 29-31, December 6, 1974.

9. Kern County APCD Test Report, Tenneco Unit 4002021, June 3, 1975.

10. "Air Pollutant Emissions Testing Report, Oil Field Steam Generators," Midway Sunset Oil Field, Kern County, CA, Chanslor-Western Oil and Development Co., Santa Fe Industries Co., Rychman/Edgerley/Tomlinson & Associates Report RETA-3216, July, 1977.

11 "Source Test, San Ardo Fields," ARB memo James J. Morgester, Chief, Enforcement Branch, to William H. Lewis, Jr., Executive Officer, dated July 28, 1977.

12. Getty Oil letter, M. L. Smith to H. J. Taback, KVB, Inc., dated June 16, 1977.

13. Test Data Sheets provided by Mobil Oil Co., San Ardo, CA, Mr. James Sklar.

14. Private communication, Mr. James Sklar, Mobil Oil Co., San Ardo, CA, August 10, 1979.

15. Private communication, Mr. Hugh Swan, Tenneco Oil Co., Bakersfield, CA, August 10, 1979.

16. Private communication, Mr. Jeff Adkins, Santa Fe Energy Co., (CWOD), Bakersfield, CA, August 10, 1979.

17. Wardner, W. R., "Annual Review of California Oil and Gas Production 1977," Conservation Committee of California Oil Producers, Los Angeles, CA, 1978.

18. Polyniak, Michael J., "Inventory of Steam Generators for Western and Central Kern County," Science Application, Inc., La Jolla, CA, August 10, 1979.

19. Private communication, Mr. Fred W. Thoits, Assistant Air Pollution Control Officer, Monterey Bay Unified APCD, Salinas, CA, August 10, 1979.

20. Sheridan, Ruth S., et al, Air Quality Impact of Proposed Oil Field Equipment in the Western Kern County Oil Fields as of July 1978," Vol. I, Science Applications, Inc., La Jolla, CA, November, 1978.

21. "Enhanced Oil Recovery Potential in the United States," U. S. Congressional Office of Technology Assessment, Washington, D.C., USGPO, Stock No. 052-003-00503-4, January, 1978.

22. McGowin, C. R., "Stationary Internal Combustion Engines in the United States," EPA-R2-73-210, April, 1973.

23. Nebel, G. J. and Jackson, M. W., "Some Factors Affecting the Concentration of Oxides of Nitrogen in Exhaust Gases from Spark Ignition Engines," presented at the Symposium on Air Pollution, American Chemical Society, New York, New York (September, 1957).

24. Aiman, R. W., "Engine Speed and Load Effects on Charge Dilution and Nitric Oxide Emissions," SAE Paper No. 720256, Detroit, MI, January, 1972.

25. Hinton, M. G., Jr., Iura, T., Meltzer, J., and Somers, J. H., "Gasoline Lead Additive and Cost Effects of Potential 1975-1976 Emission Control Systems," SAE Paper No. 730014, SAE Congress, Detroit, MI, January, 1973.

26. R. J. Ferb letter to H. J. Taback, June 26, 1979, regarding scrubbing equipment for steamflood boilers in Southern California.

27. "New Processes and Technology Alert," Chemical Engineering, January 16, 1978, Vol. 85, No. 2, p.149.

28. Orians, Michael (Ed), "Sulfur Dioxide/Sulfate Control Study," Executive Summary, SCAQMD, Los Angeles, CA, May, 1978.

29. California Air Resources Board, Staff Report No. 78-7-1, April 26, 1978, "Consideration of a Proposed Model Rule for Control of Emission of SO_x and NO_x from Steam Generators in the San Joaquin Valley Air Basin."

30. Coleman, Richard, California Thermal Oil Utilization, Vol I, Executive Summary, DOE Contract ET-78-C-03-1864, September 5, 1979, Page 1.

31. Ibid, Page 25.

32. Ibid, Page 4.

33. Cantrell, Jr., C. J., "A Brief Synopsis of the John Zink Low NO_x Steam Generator for Recovery of High Viscosity Crude," prepared for ARB.

34. Holliday, George, "Statement on Behalf of Ad Hoc NO_x Study Group Before the CARB Public Hearing . . . Bakersfield, CA, March 5-6, 1980."

35. Faucett, H.L., et al," Technical Assessment of NO_x Removal Processes for Utility Applications," EPA Report 600/7-77-127.

36. Jones, G. D. and Johnson, K. L., "Technology Assessment Report for Industrial Boiler Applications; NO_x Flue Gas Treatment," EPA Report 600/7-79-178g, December, 1979.

37. Ando, J., "NO_x Abatement for Stationery Sources in Japan," EPA Report 600/7-79-205, August, 1979.

38. Landes, Terry, Unpublished data from the Kern County Air Pollution Control District, received April 24, 1980.